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CENTER

CRDEC-TR-028

SELECTION AND EVALUATION OF A REAL TIME MONITORING SYSTEM FOR THE BIGEYE BOMB FILL/CLOSE PRODUCTION FACILITY (PHASE II)

Foy E. Ferguson
Michael W. Ellzy
RESEARCH DIRECTORATE
Joseph W. Lovrich
MUNITIONS DIRECTORATE
Theodore L. Strozyk, Jr.
DETECTION DIRECTORATE

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U.S. ARMY
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MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

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From April 1985 through August 1986, detection studies for a monitoring system for Phase II Binary facilities were conducted. This project was to provide the technical information for effectively monitoring the workplace for personal protection in the Phase II production facilities. The contractors for the ethyl-2-diisopropylaminoethyl-methylphosphonite (QL) production facility and the Bigeye fill/close facility have the overall responsibility for design, construction, and prove-outs of these facilities and subsequent production, including detection and monitoring. This effort, which was sponsored by the Munitions Directorate and technically evaluated by Research Directorate, was directed by Detection Directorate's Development Division Chairman, who headed a committee of representatives of the major activities of the U.S. Army Chemical Research, Development and Engineering Center, specifically assembled for this purpose. The committee recommended using the PA 260 gas analyzer as the generic phosphorous detector in the Phase II facilities and the MIRAN 80 for monitoring (continued on reverse)

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diisopropylaminoethanol (KB), which is not a phosphorous compound. This report documents the initial detection studies done by Research Directorate for the Phase II Binary facilities.

PREFACE

The work described in this report was authorized under Project No. 1L162706A553A, Chemistry and Effects of Threat Agents. This work was started in April 1985 and completed in August 1986. The experimental data are contained in laboratory notebooks 86-0111, 86-0023, 86-001, 9874, and 9743.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for release to the public.

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1.1 Objective.

This report documents the detection studies conducted for monitoring O-(2-diisopropylaminoethyl) O'-ethyl(2-diisopropylaminoethyl) methylphosphonite (QL) and its degradation products for the purpose of personal protection in the workplace. These findings will be provided to the contractors of both the QL production facility and the Bigeye fill/close facility as advisory guidance These development studies were conducted at the U.S. Army Chemical Research, Development and Engineering Center (CRDEC) from April 1985 through August 1986 for the Phase II Binary Program.

1.2 Background.

1.2.1 Chemicals Evaluated.

In planning prior to FY85, the development of the detection and monitoring system required for the Phase II binary program was to be tasked to the Phase II final design contractor for the QL production facility because it was the leading facility effort at that time. In FY85, the Bigeye fill/close facility became the leading facility effort when it received the required funding for the final design. At about the same time, the decision was made to perform as much of the detection and monitoring development work as possible in-house in an effort to keep certain key areas moving until a final design contract for the QL production facility could be awarded. One of the obvious problems was a determination of what compounds would be monitored and at what concentration levels. Toxicological testing was to begin with QL, O,O'-diethylmethylphosphonite (TR), methyldichlorophosphite (SW), O,O'-bis(2-diisopropylaminoethyl) methylphosphonite (LT), triethylphosphite (TEP), and diisopropylamino-ethanol (KB) as agreed to by The Surgeon General in September 1984. The determination of which compounds were to be tested was based on the greatest potential for worker exposure; that is, raw materials (KB), intermediate products (TR and SW), waste products (LT and TEP), and final product.

1.2.2 Monitors Initially Recommended for Evaluation.

Based on an assumed requirement to monitor the compounds mentioned above, a survey of existing monitoring systems was conducted by Research Directorate, CRDEC, from April to July 1984. The three most feasible detector candidates for the Phase II programs were the Automatic Continuous Air Monitoring System (ACAMS), Automatic Chemical Agent Detector/Al m (ACADA), and Hydrogen Flame Emission Detector (HyFED). Subsequent to performing the survey, a Phase II Detection and Monitoring Committee was formed in-house

to address the requirements in this area and to test the equipment; that is, the same approach that was successfully used during the Phase I Binary (Difluoro) detection and monitoring development efforts. The committee reviewed and concurred in the findings of the survey and agreed with a requirement for feasibility testing of the three candidates to determine which one was best suited for the specific Phase II applications. However, the problem relating to the concentration levels at which to monitor were dependent on the results of toxicological studies that were on-going for QL and, in some instances, not even started for the QL process compounds. In addition, it was recognized that the lack of permissable exposure limits (PEL) would complicate the ACAMS effort in regard to such things as to whether preconcentrators had to be used, what type, etc. The decision was made to establish minimum detectable limits for each system (ACAMS, ACADA, and HyFED) for each compound undergoing toxicological testing. (Note: SW was excluded from the toxicological testing because the primary inhalation hazard associated with this compound is the degradation product hydrogen chloride for which sufficient technological data exists and a commonly used industrial detector for chlorine could be used for monitoring in these instances.)

1.2.3 Monitoring for Specific Organophosphorus Compounds versus Monitoring for Total Phosphorus.

Near/Mid Range Munitions Producibility Branch (Munitions Directorate, CRDEC) personnel reviewed the test methods, analytical procedures, and data related to recent toxicology tests (acute and subchronic) with QL. Their results indicated that the toxicity data being developed is not related to the specific compound, QL, but rather the combination of QL and/or its degradation products, O-ethyl methylphosphi'nate (YL); KB; O-(2-diisopropylaminoethyl) methylphosphinate (QA); and O,O ethyl 2-diisopropylaminoethyl methylphosphonate (QB). Because QL degrades in the presence of atmospheric moisture and oxygen, the tests are considered valid and representative of a "real world" scenario with relation to potential worker exposure. However, the problem arises in developing detection and monitoring capabilities in that little, or none of the specific material (in this case QL) may be present even though some biochemical responses (cholinesterase depression) may still occur. [Note: This same problem could arise with the other compounds (TR, LT, and TEP) for which tests are just being initiated.] As a result, the development of a detector for specific compounds, as was planned, did not seem feasible. The two detectors having the capability for detection of the specific compounds, which were proposed for further study, were the ACAMS and the ACADA. The generic detector being considered was the HyFID.

Personnel of the Near/Mid Range Munitions Producibility Branch hosted a meeting with representatives of the Toxicology Division (Research Directorate, CRDEC) and the Health and Veterinary Services Office (HVSO), CRDEC, to surface these concerns. The principal objective of the meeting was to mutually agree on whether development of a detection capability for specific compounds (QL, TR, LT, TEP, etc.) was still feasible or whether future development should be steered to nonspecific (generic) detection capabilities; for example, total phosphorous bearing compounds.

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A more prudent approach to detection and monitoring requirements at the Phase II binary facilities is to monitor for a phosphorus equivalent concentration. Such an approach could essentially provide the total concentration of organophosphorus constituents regardless of the individual makeup of degradation products that might be present. The PEL would also have to be established using this approach (phosphorus equivalent concentration). Since four organophosphorus compounds (QL, TR, TEP, and LT) will undergo toxicity testing, the final PEL established would be based on the phosphorus-equivalent of the compound that was demonstrated to be the worst toxic hazard. The PEL recommended to The Surgeon General would be based on this approach.

There was no assurance that The Surgeon General would accept this approach. One option would be to accept the recommended approach with an additional requirement to identify the individual compound(s) present that may be setting off alarms. Because HyFeed (phosphorus detector) development would require supplemental support efforts with gas chromatography (GC), it was thought that sufficient information could be generated with both systems to provide a capability to determine the total phosphorus equivalent concentration using the HyFED, as well as identification of individual compounds by GC. [Note: GC was the primary analytical instrument used during production operations (including QL) at Newport Army Ammunition Plant (AAP) during the 1960s and has been used extensively at CRDEC for the analysis of QL and similar compounds since that time.] The attendees thought the adequacy of the ACADA for the currently proposed application was very doubtful. Near/Mid Range Munitions Producibility Branch personnel agreed to meet with the experts on the ACADA to verify its adequacy.

It was noted that a separate detector, which contains no phosphorus and would not be detected by the HyFED in its current configuration, may be required to monitor for KB. Preliminary results of toxicology tests indicated that KB was positive in three mutagenicity assays. As a result, it was agreed to evaluate the MIRAN 80 and MIRAN 980 detectors for the detection of KB. These detectors are both "off-the-shelf" items produced by the Foxboro Company, Norwalk, CT.

1.2.4 Evaluation of ACADA for Detection and Monitoring at the Phase II Binary Facilities.

Detection Directorate personnel indicated that upon carefully weighing all information currently available on detection and monitoring for binary facilities and after lengthy consultation with Dr. Glenn Spangler of Allied Bendix, an expert in the field of Ion Mobility Spectrometry (IMS), a generic detector such as HyFED offered the highest probability of successfully developing a detection and monitoring system for binary facilities. The very characteristic that made ACADA so attractive as a chemical agent detector, for example, the capability to detect and identify specific agents, made it undesirable for use in the binary facilities. The IMS technology used in ACADA did not permit the detection of a chemical component based on its chemical reactions (such as is needed when detecting toxic chemical groups) but rather relied on the mass of the end Products formed. As toxicity studies indicated that the toxic hazard at a binary facility would come from a number of different chemical substances as well as QL, the ACADA or any other compound specific detector would have to accurately quantify each compound and

subsequently integrate this data in the presence of a myriad of interacting materials. Although the ACADA had the capability to quantify, the accuracy achievable would not be acceptable for the detection and monitoring of a binary facility. The capability of ACADA or any compound specific detector to meet the hazardous materials detection requirements needed to adequately protect binary facilities was highly questionable, and it was dropped from consideration for further evaluation.

2. MANAGEMENT

The in-house binary group was established to manage the development studies of the Phase II Bigeye detection and monitoring system. Chairmanship for this group was assigned to the Detection Directorate representative. This position had responsibility for overall management, program structure, implementation, and coordination of all cost documents. Representatives from Research Directorate led the major in-house investigative efforts for evaluation of candidate Phase II Bigeye monitors, sampling system, and calibration concepts with support from Detection Development Division, Detection Directorate. As specific situations of workload warranted, ad hoc members were added to the group on an interim basis.

3. PA 260 EVALUATION

3.1 Description of the PA 260 Detector.

The PA 260 detector is manufactured and distributed by Colmmbia Scientific Industries Corporation (CSI), Columbus, OH. It is a self-contained, real-time, continuously operating dry flame photometric detector (FPD), specific for compounds containing phosphorus. In comparison to compounds lacking this element its response is 10,000:1 (phosphorus to non-phosphorus). Compounds containing phosphorus emit bands of visible light when burning in a hydrogen rich flame. Narrow band-pass filters isolate specific wavelengths (e.g., 525 nm for phosphorus), thereby creating the unique selectivity of this detector for such compounds. The PA 260 is comprised of four basic subsystems: (1) the pneumatics (2) the FPD burner assembly (3) a photomultiplier tube assembly and (4) the associated electronics.

Figure 1 represents the pneumatic network of the detector in its most simplistic form. During normal sampling of airborne materials, the sample enters the unit through the back, using either direct or indirect metered inlets. If direct, the sample flows immediately to the burner block. Hydrogen is supplied to the unit through an inlet also located in the back of the unit. The hydrogen pressure regulated at 45-60 psig is sent through a temperature controlled capillary and routed directly to the burner block. The controlled hydrogen flow provides a stable flame in environments with larger temperature fluctuations.

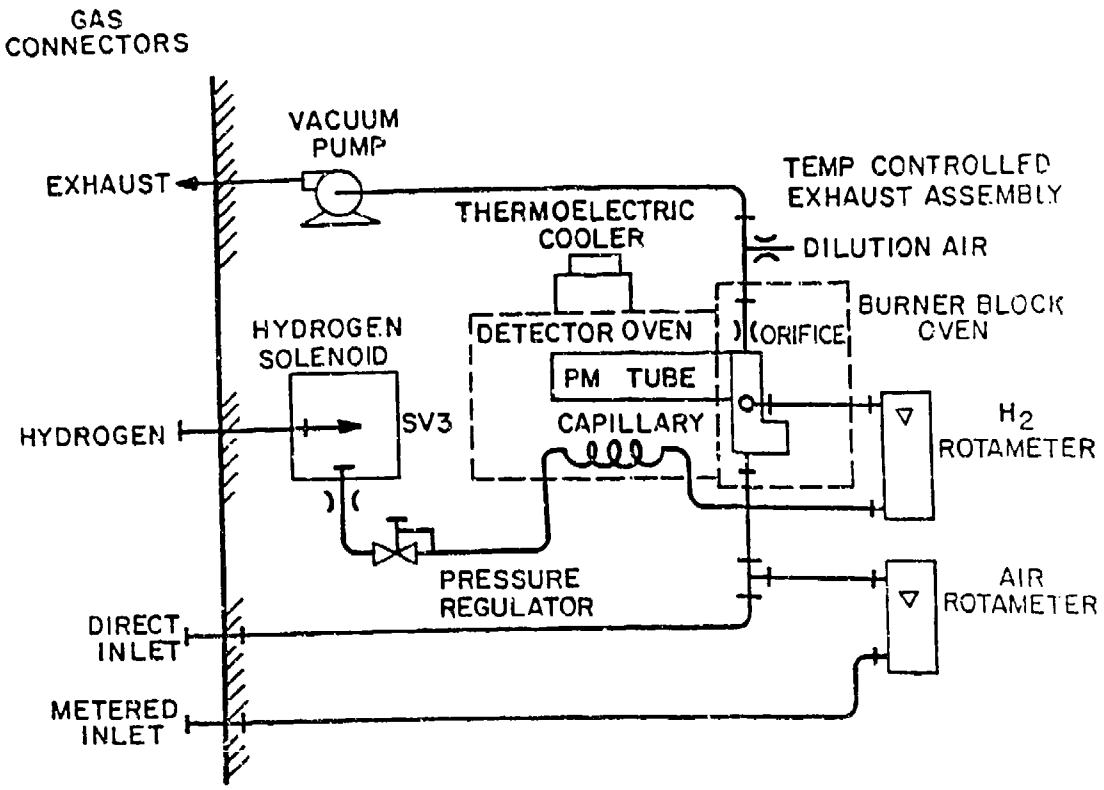


Figure 1. PA 260 Detector Pneumatic Network

The burner block assembly provides the reaction chamber for the combustion of phosphorus containing compounds and subsequent chemiluminescent emissions. Its purpose is to produce a stable burning condition for the flame. Sample laden air is introduced to the burner block at the bottom and is mixed with hydrogen at the side. The gases are mixed and sent through a special burner tip, combustion occurs, and by-products are exhausted out the top of the block. The temperature of this block assembly is maintained at approximately 150 °C. A flame sensor is provided to warn of flame out conditions and contains circuitry for a relight signal.

The PA 260 electronic system processes the signal emanating from the FPD readout. An output signal from the photomultiplier (PMT) in the form of an electrical current is fed to an amplifier, which converts the current to a voltage. The output signal from the FPD is an exponential function that is plotted linearly on log-log paper. The log response is adjustable so that the voltage output may represent up to six decades of input current. Using this log-normal mode of operation (See Appendix A), a wide dynamic range is obtained with good readability for low concentrations.

3.1.1 Baseline Stability.

To determine drift of the PA 260, the detector was operated while connected to a Perkin-Elmer strip chart recorder and a Hewlett Packard, model 110, digital voltmeter, both equipped with 0-1 volt input. These tests were run under ambient laboratory conditions. The detector was run for three consecutive days while connected to a charcoal canister that is supplied with the unit. This was done to provide zero air to the analyzer. The detector was operated in a log-normal mode during the entire test. The instantaneous response of the PA 260 monitor with time is indicated in Tables 1-3. No measurable drift in detector response to zero air was observed during 72 hr of testing. Drifts during the test were never greater than 0.6% standard deviation for any given day.

Table 1. PA 260 Detector, Baseline Stability Test - Day 1

Test No.	Amps x 10^{-8}	Time (hr)
1	1.72	1
2	1 717	
3	1.74	
4	1.70	
5	1.75	
6	1.748	
7	1.739	
8	1.780	8
9	1 975	
10	1.788	
11	1 780	
12	1.780	
13	1.788	
14	1.782	
15	1 788	
16	1 514	
17	1.788	
18	1.787	
19	1.782	
20	1.788	
21	1.780	
22	1 770	
23	1 730	
24	1.738	24

M = 1.764 x 10^{-8}
S.D. = 0.0015
% SD = 0.4

Table 2. PA 260 Detector, Baseline Stability Test - Day 2

Test No.	Amps x 10^{-8}	Time (hr)
1	1.746	25
2	1.718	
3	1.728	
4	1.720	
5	1.728	
6	1.730	
7	1.730	
8	1.738	
9	1.734	
10	1.742	
11	1.706	
12	1.710	
13	1.722	
14	1.726	
15	1.718	
16	1.738	
17	1.726	
18	1.742	
19	1.742	
20	1.512	
21	1.780	
22	1.774	
23	1.786	
24	1.840	48

M = 1.742×10^{-8}
S.D. = .0015
% SD = 0.6

Table 3. PA 260 Detector, Baseline Stability Test - Day 3

Test No.	Amps x 10^{-8}	Time (hr)
1	1.787	49
2	1.125	
3	1.778	
4	1.663	
5	1.742	
6	1.726	
7	1.738	
8	1.718	
9	1.726	
10	1.722	
11	1.710	
13	1.742	
14	1.734	
15	1.738	
16	1.730	
17	1.824	
18	1.762	
19	1.700	
20	1.675	
21	1.694	
22	1.889	
23	1.774	
24	1.660	72

M = 1.742×10^{-8}
S.D. = .0012
% SD = 0.5

3.1.2 Safety of the PA 260 Detector.

The PA 260 detector is a completely self-contained unit that is considered safe to operate under normal operating conditions. The detector designer, CSI, tried to minimize the hazards to personnel and equipment. These hazards include electrical shock, pinch points, fire, and explosion due to the use of hydrogen gas.

Electrical and pinch hazards were minimized by totally enclosing electrical components and moving parts within the unit. Furthermore, the design ensures that external parts and surfaces of the analyzer are at ground potential during normal operations. CSI minimized the fire and explosion hazards by incorporating safety design features in the PA 260 detector. These safety design features can be summarized as follows:

a. An orifice (snubber) is placed in series with a hydrogen shut-of solenoid valve to limit the hydrogen gas flow to a maximum of

300 cm^3/min should a leak develop within the analyzer. An additional orifice can be installed at the cylinder regulator to prevent high overflows (i.e., over 600 cm^3/min).

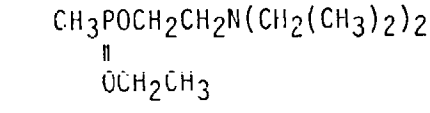
b. A normally closed, soleroid valve located in the rear panel provides internal shut-off of the hydrogen gas flow if the flame is not lit or if there is a power failure. The valve is only energized when the ignitor button is pushed or a flame-on condition is indicated.

c. During ignition of the air/hydrogen mixture, flash back of the air/hydrogen mixture in the burner block is prevented by an integral 7 mL capillary in the hydrogen line. The flame front cannot be maintained through this smaller but critical flow path.

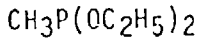
3.2 Experimental Techniques and Discussions.

The susceptibility of QL to hydrolysis and disproporticnation is dependent on the amount of moisture present. QL is hydrolyzed primarily to KB and YL. If disproportionation occurs, the major products are TR and LT caused by silmultaneous oxidation and reduction. These routes are shown below.[1]

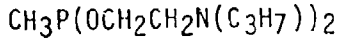
A. Disproportionation



QL

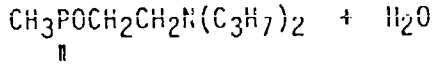


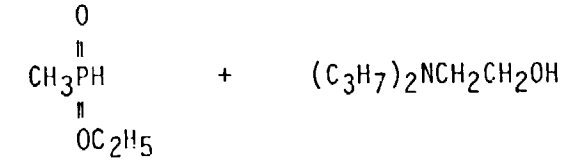
TR



LT

B. Hydrolysis





YL KB

[1]Grula, Robert J., and Armelie, Dominic, The Effect of Added Impurities on the Thermal Stability of QL, EC-TR-76085, Edgewood Arsenal, Aberdeen Proving Ground, MD, December 1976, UNCLASSIFIED Report. (AD B015 613L)

Depending upon the extent of disproportionation or hydrolysis, other products may be formed including QB, O-(diisopropylamino ethyl) ethylmethyl-phosphinate (QC), O-ethyl (diisopropylamino ethyl) methyl-phosphonate (QD), O-O-bis (diisopropylamino ethyl) methyl-phosphonate (LTO), ethanol (C_2H_5OH), and O,O-diethylmethylphosphonate (TRO).

From the onset of this investigation it was obvious that to study such a complex mixture, analytical tools such as gas chromatography, mass spectrometry, NMR spectroscopy, and infrared spectroscopy were paramount to any meaningful evaluation.

The major thrust of this experimental effort was to (1) determine whether QL and its related products could be detected by the HyFED, model PA 260, (2) if feasible, determine if dynamic standards of QL and related products could be generated and collected in some suitable media, and (3) determine if the PA 260 could detect the compounds of interest at the threshold limit values (TLVs) required and be modified to detect simultaneously non-phosphorus containing compounds at 0.03 mg/m^3.

It was equally important that very strict conditions be established and maintained for humidity, dissemination, collection, and selective monitoring for QL and its related products To accomplish these tasks, it was necessary to establish GC methods tc determine the purities of the QL and the other components to afford a reference data base for these compounds.

3.2.1 GC Methods - Determination of Response Factors for QL TR, TEP, KB, YL, and LT.

High purity samples, as determined by GC and nuclear magnetic resonance (NMR) of QL, TR, TEP, KB, YL, and LT were obtained from Munitions Directorate, CRDEC. A comparison of the purities determined by GC and NMR of these samples is contained in Table 4.

Table 4. GC/NMR Analysis of QL and Related Compounds

Compound	23 Oct 85 GC Results*	24 Oct 85 NMR Results
QL	95.87	94.2
TR	92.53	99.2
KB	99.37	59.9
**YL	49.58	94.8
TEP	97.25	94.4
LT	94.92	

*Samples were run in triplicate.
**This compound was used for qualitative purposes but was later redistilled.

The initial and most practical approach for the assessment of these compounds was to use proven methods of analysis. Standard GC columns containing solid supports coated with liquid phases such as SE-54, SE-52, OV 101, OV 17, and various conforms of these phases, proved to be adequate for analysis of large samples injected onto these columns. However, when very small sample amounts representing nanogram quantities were injected, peak broadening was experienced; and in some cases, total loss of resolution was observed. Note that one of the primary objectives was to measure these compounds in the parts-per-million to parts-per-billion ranges. Based on this information and our findings, further attempts to use these columns were abandoned. It is our opinion that the poor performance of these columns for trace analysis was due to the large surface area that is characteristic of diatomaceous materials used in most standard GC columns.

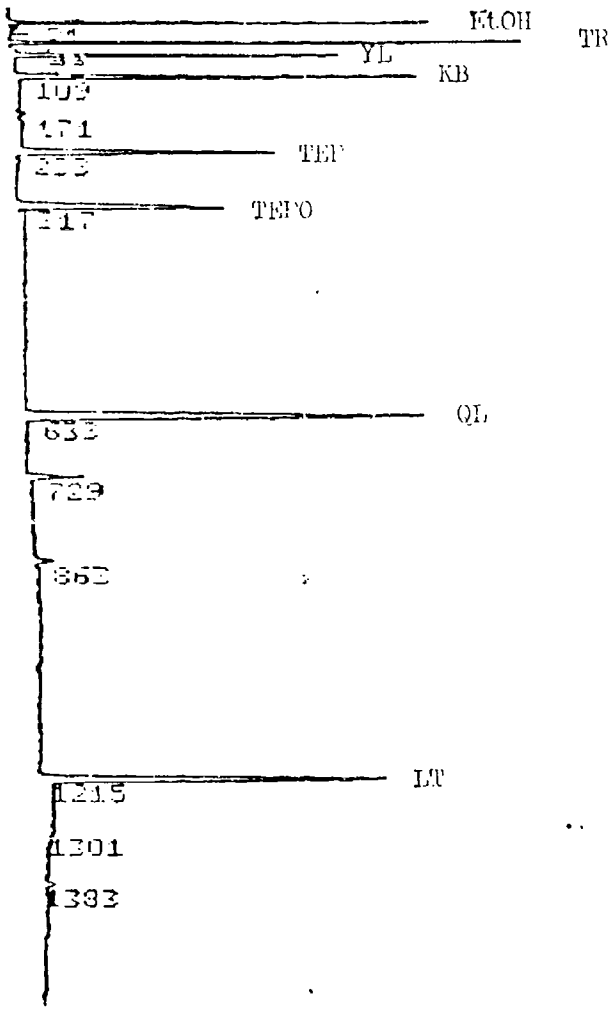
The obvious choice was to investigate methods of minimizing or eliminating this surface effect. This was accomplished by selecting wall coated capillary megabore columns, which did not contain diatomaceous material or any other solid support. A 15-m DB-5 capillary column was installed in a Varian 3700 series GC. Samples of the candidate materials were analyzed on this system, which proved to be suitable for both neat and trace analysis. A typical chromatogram of QL and the degradation products of interest are included in Figure 2. Resulting response factors (Table 5) for the chromatograph were determined. Complete and reproducible resolution was obtained. Operating parameters used in these experiments are contained in Appendix B.

Table 5. Response Factor Table (QL and Related Compounds)

Compound	Retention Time (s)	Peak Area	Connected Sample Wt (g)	Wt %	KF Factor
EtOH	21	2637	0.1146	3.60	1.902
TR	53	5800	0.4645	14.57	3.501
YL	73	5330	0.2941	9.22	2.410
KB	109	9312	0.4272	13.40	2.005
TEP	233	7965	0.4531	14.72	2.575
TEPO	317	9624	0.5337	16.74	2.424
QL	635	18840	0.4246	13.52	1.000
QA	729	1788			1.001*
QC	863	591			0.998*
LT	1217	16305	0.4170	13.08	1.118

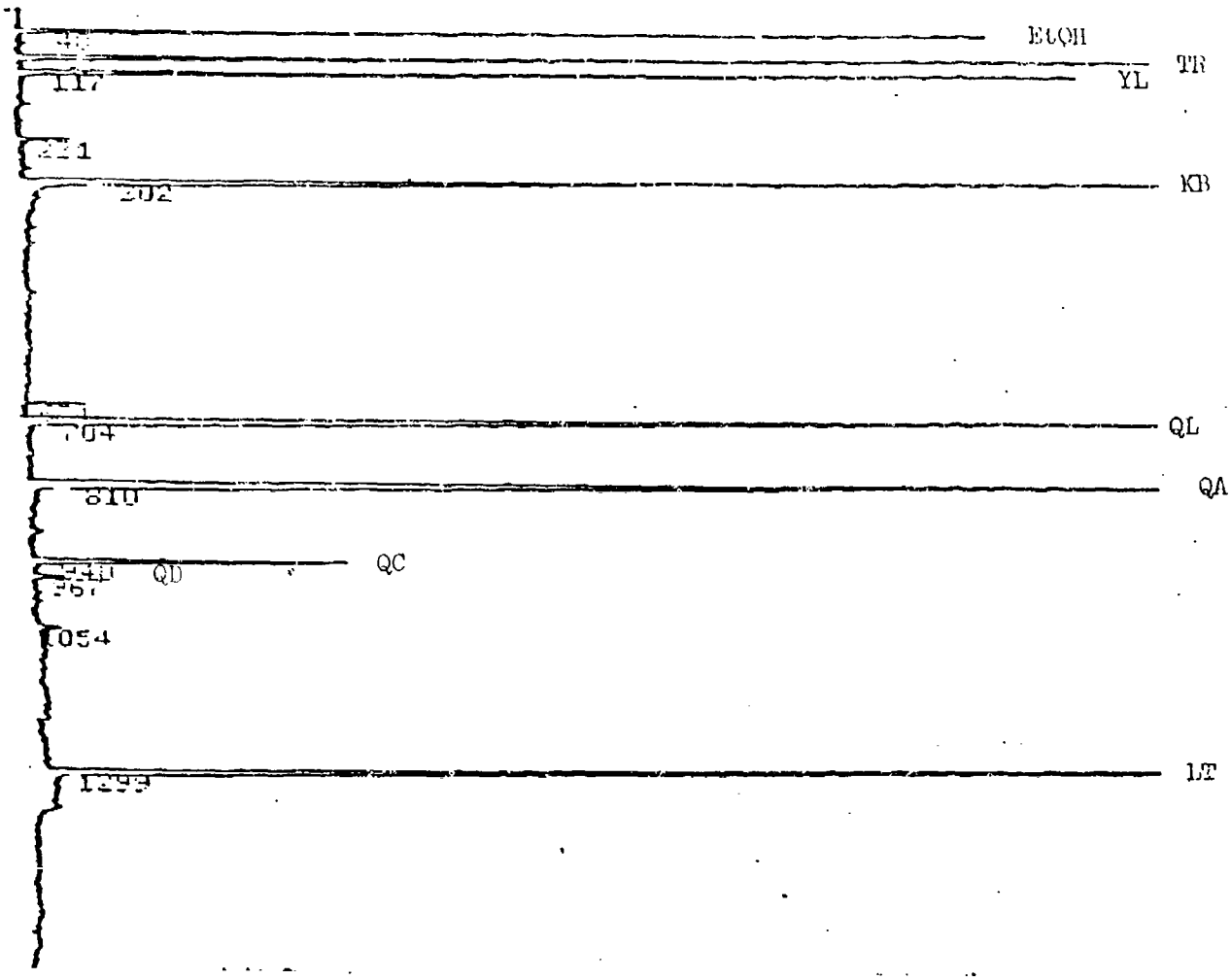
*Calculated Response Factors

After satisfactory results were obtained using the DB-5 column, calibration mixtures were prepared and chromatographed (Figure 3).



	COMPOUND	AREA %	RT	Area
1	EtOH	3.346	21	2637
2	TR	7.36	53	5800
3	YL	6.764	73	5330
4	KB	11.82	109	9312
5	TEP	10.58	233	8336
6	TEPO	12.91	317	10170
7	QL	23.63	633	18620
8	QA	2.18	729	1718
9		.82	863	646
10	LT	20.27	1215	15969
11		.335	1383	264
TOTALS		99.98		78802

Figure 2. FID (GC) Analysis of Calibrated QL Mixture



CHANNEL 1 RUN 5 FILE 1 METHOD 0

INDEX 4 SAMPLE 2

PEAK #	COMPOUND	AREA %	RT	AREA
1	ETOH	3.077	48	2092
2	TR	8.106	92	5512
3	YL	5.084	117	3457
4		.39	231	265
5	KB	14.61	302	9937
6		.091	674	62
7	QL	26.84	704	18255
8	QA	20.34	810	13832
9	QC	2.918	940	1984
10		.221	967	150
11		.165	1054	112
12	LT	18.15	1299	12342
TOTALS		99.99		68000

Figure 3. FID (GC) Analysis of Deteriorated QL Sample

A typical calibration mixture and the resulting calculated correction factors are shown in Table 6.

Table 6. QL and Related Compounds Calibration Mixture

Component	wt of Component (g)	Corrected wt of Component (g)	wt % of Components
YL	0.3569	0.2941	9.22
KB	0.4303	0.4272	13.40
QL	0.4460	0.4246	13.52
TR	0.4947	0.4645	14.57
TEP	0.4826	0.4531	14.72
TEPO	0.5348	0.5337	16.74
LT	0.4422	0.4170	13.08
EtOH	0.1146	0.1146	3.60

The correction factor calculations are based on equation 1. Once determined, the response factors were used to calculate the weight Percent concentration as shown in equation 2 for all subsequent analyses (see Tables 6 and 7).

Table 7. Example of Purity Analysis

Compound	KF Factor		Area i		Corrected Area i		% Conc
EtOH	1.902	X	2092	=	3,978.98	=	3.996%
TR	3.501	X	5512	=	19,297.50	=	19.121%
KB	2.005	X	9937	=	19,923.70	=	19.742%
YL	2.410	X	3457	=	8,331.37	=	8.255%
QL	1.000	X	18,255	=	18,255.00	=	18.088%
QA	1.001	X	13,832	=	13,845.83	=	13.706%
QB	.998	X	1984	=	1,980.03	=	1.962%
QC	.998	X	150	=	149.70	=	0.148%
LT	1.118	X	12342	=	13,798.36	=	13.672%
					99,560.47		98.685%

$$\% \text{ LT} = \frac{1.118 \times 12{,}342}{99{,}560.47} \times 98.65 = 13.67$$

$$K_iF_i = \frac{Conc_i \times Area_i}{Area_i \times Conc_{is}} \quad (1)$$

Where, K_iF_i is the correction factor.

$Conc_i$ is the amount of pure component$_i$ in the calibration sample.

$Area_{is}$ is the area of component selected as the KF reference peak in the calibration sample.

$Conc_{is}$ is the amount of component selected as the KF reference.

$Area_i$ is the area of pure componenti in the calibration sample.

$$\% Conc_i = \frac{KF_i \times Area_i \quad (XF)}{\sum_{i=1}^{n} (KF_i \times Area_i)} \quad (2)$$

Where, $\% Conc_i$ is the percent of components in the analysis sample.

XF is the total percentage of the analysis sample represented by the components that are not accounted for if less than 100.

KF_i is the calibration factor for component i calculated in the analysis run.

$Area_i$ is the area of the componentsi Peak in the analysis.

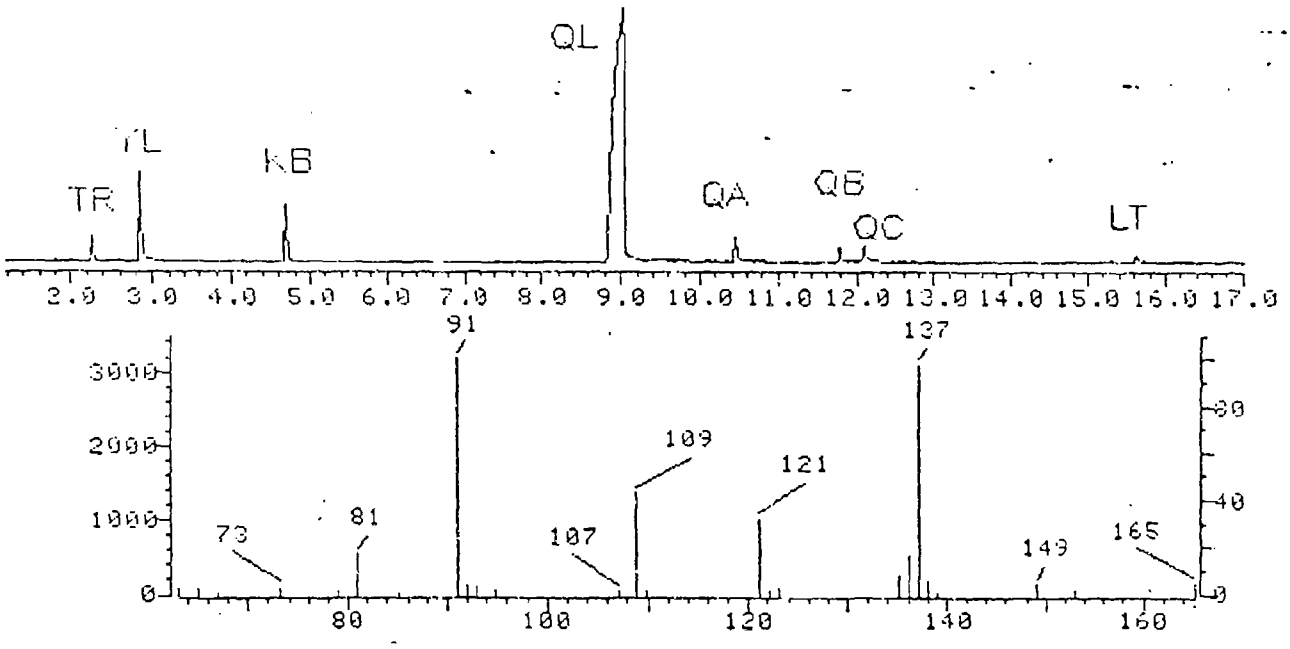
3.2.2 GC/Mass Spectrometry Methods - Spectral Data for TR, YL, KB, QL, QA, QB, QC, and LT.

Much of the data obtained during the development of GC methods has provided valuable information in development of the following GC/MS methods. A Hewlett Packard GC/MS, model 5985B, fitted with a J&W DB-5, 30 m x 0.25 mm id capillary column interfaced directly into the ion source was used throughout this investigation. The same column type was used in the GC methods.

The thrust of this investigation became more important after obtaining responses on the PA 260 when challenged with the effluent from the diffusion generator containing high purity QL. It was necessary to confirm the existence of QL vapor by MS since all attempts to collect QL in a suitable solvent with subsequent GC analysis were unsuccessful, as explained in section 3.3.3.

Chromatographic and mass spectral data were collected for liquid QL and its degradation or related products. QL spectral data was obtained for both liquid and vapor forms. The data was arranged as follows (see Figures 4-12):

QL STD CI:Methane

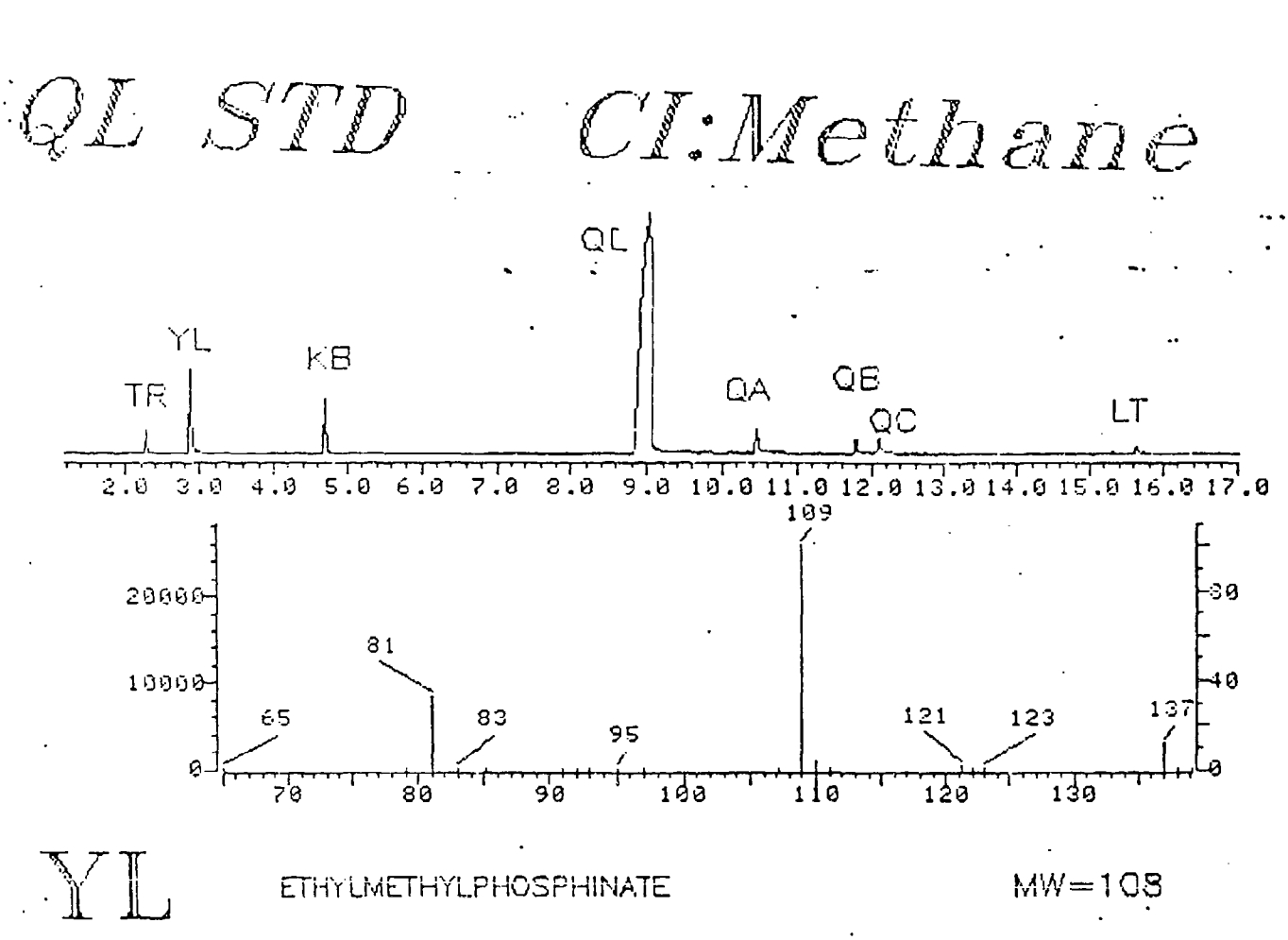


TR O,O'-DIETHYLMETHYLPHOSPHONITE MW=136

m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
62.95	2.30	81.05	16.92	95.00	1.89	122.05	1.86	138.05	5.69
64.95	2.18	85.05	.11	107.15	1.36	123.05	2.62	139.05	1.04
67.05	.43	91.00	100.00	109.20	42.69	135.05	7.96	149.05	4.37
73.05	2.76	92.00	4.04	109.90	1.89	136.05	16.08	153.05	1.07
79.05	1.76	93.00	3.28	121.15	32.26	137.05	97.34	165.15	4.64

Move cursor; then press carriage return :

Figure 4. MS Spectra for O,O'Diethylmethylphosphonite (TR)

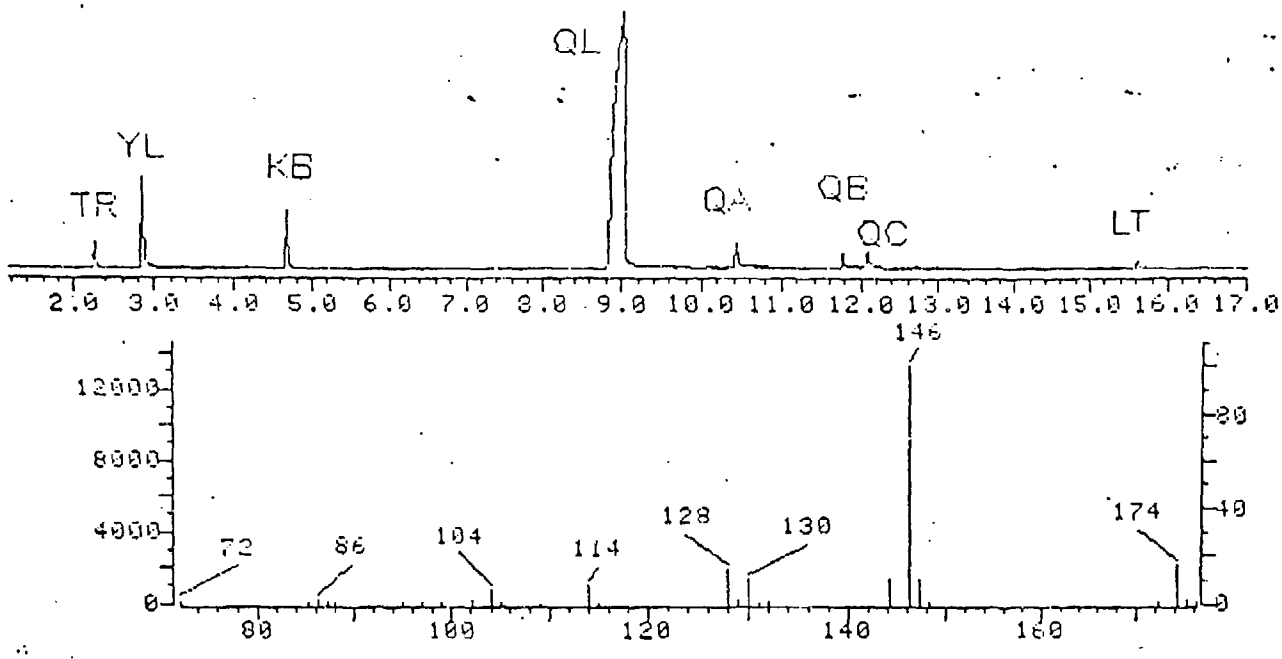


m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
64.95	.18	85.05	.05	95.00	.40	110.00	3.68	123.05	.23
79.05	.17	91.00	.15	97.00	.05	111.00	.46	137.05	11.77
81.05	32.64	92.00	.15	107.15	.63	121.15	1.57	138.05	.72
83.05	.09	93.00	.30	109.00	100.00	122.05	.07	139.05	.14

Move cursor; then press carriage return :

Figure 5. MS Spectra for O-Ethylmethylphosphinate (YL)

QL STD CI:Methane



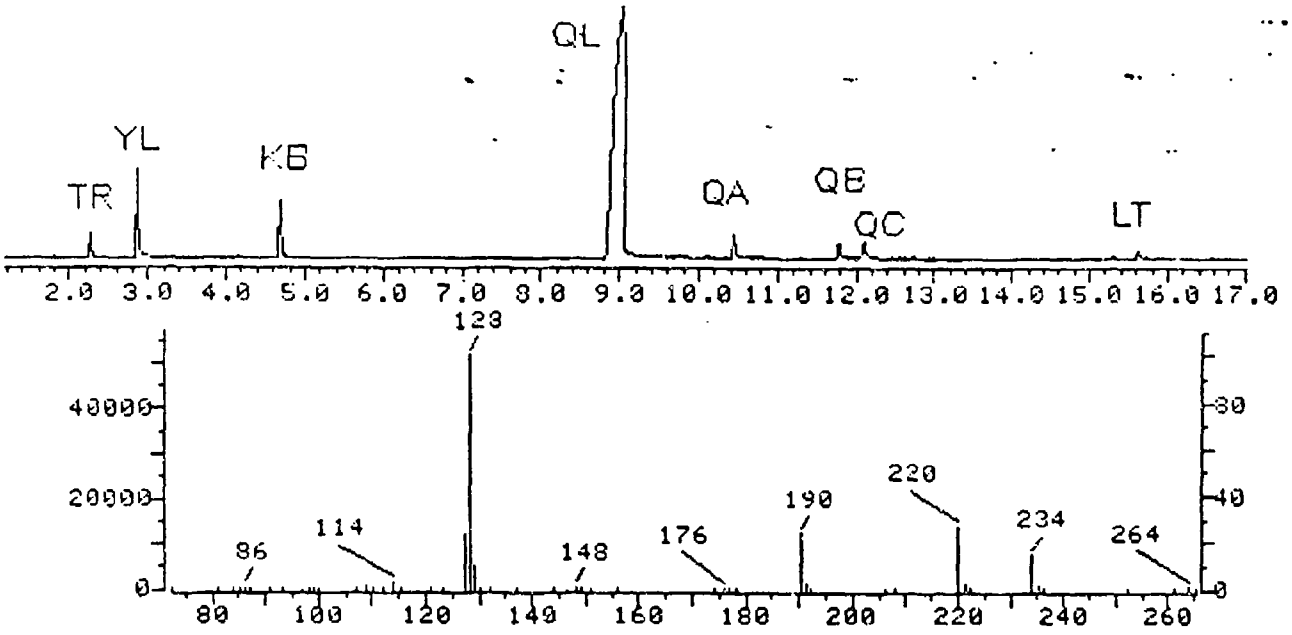
KB 2-DIISOPROPYLAMINOETHANOL MW=145

m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
72.05	.71	97.00	.23	114.15	7.47	131.05	.88	148.20	.67
85.20	.11	99.00	.11	115.15	.77	132.05	.60	172.15	.17
86.05	1.12	102.15	1.23	128.05	13.72	144.20	9.67	174.25	15.65
87.05	.17	104.15	5.42	129.20	1.81	146.20	100.00	175.15	2.00
88.00	.26	105.00	.39	130.05	9.52	147.20	9.42	176.15	.18
95.00	.17	109.00	.03						

Move cursor; then press carriage return :

Figure 6. MS Spectra for 2-Diisopropylaminoethanol (KB)

QL STD CI:Methane



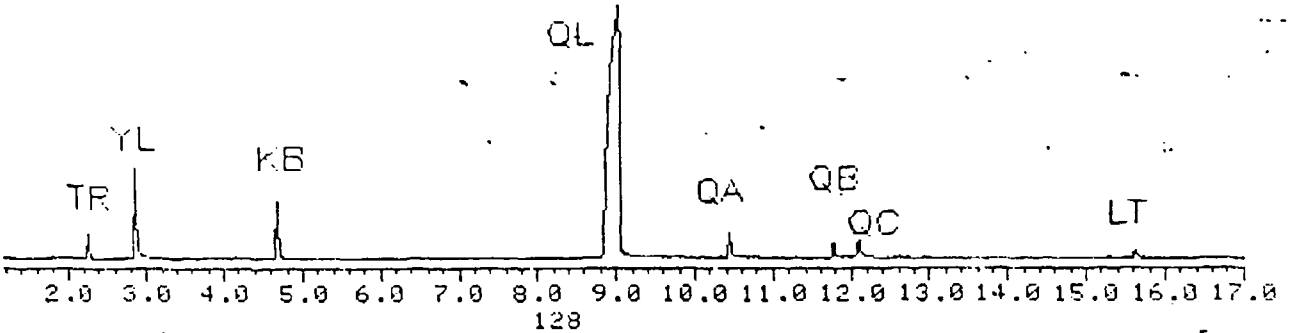
QL ETHYL(2-DIISOPROPYLAMINOETHYL)METHYLPHOSPHONITE MW=235

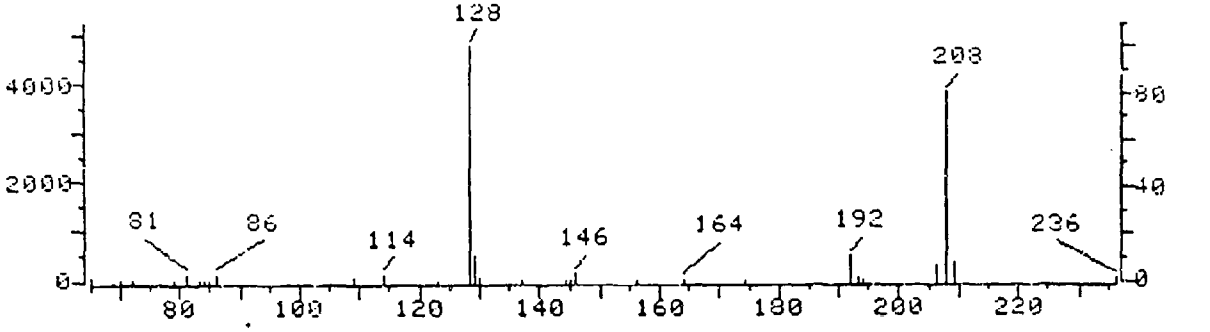
m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
72.05	.13	100.15	.07	128.20	100.00	156.20	.32	220.20	26.88
81.05	.28	107.00	.06	129.05	9.42	174.15	.06	221.20	3.12
84.05	.74	109.00	1.89	130.05	.41	176.15	.29	222.20	.37
85.20	.76	110.15	.06	132.05	.08	177.15	.09	234.15	14.87
86.05	.89	112.15	.90	137.05	.60	178.15	.08	235.15	2.07
87.05	.09	114.15	3.11	144.20	.06	190.15	23.99	236.25	.72
91.00	.05	115.15	.26	146.20	.02	191.15	2.47	252.25	.11
93.00	.04	121.00	.09	148.05	.88	192.05	.82	261.05	.06
97.00	.00	123.05	.03	149.05	.34	206.20	.24	264.20	1.46
98.15	.45	127.20	23.18	151.05	.05	208.20	.09	265.20	.23

99.15 Move cursor; then press carriage return :

Figure 7. MS Spectra for Ethyl(2-Diisopropylaminoethyl) Methylphosphonite (QL)

QL STD CI:Methane





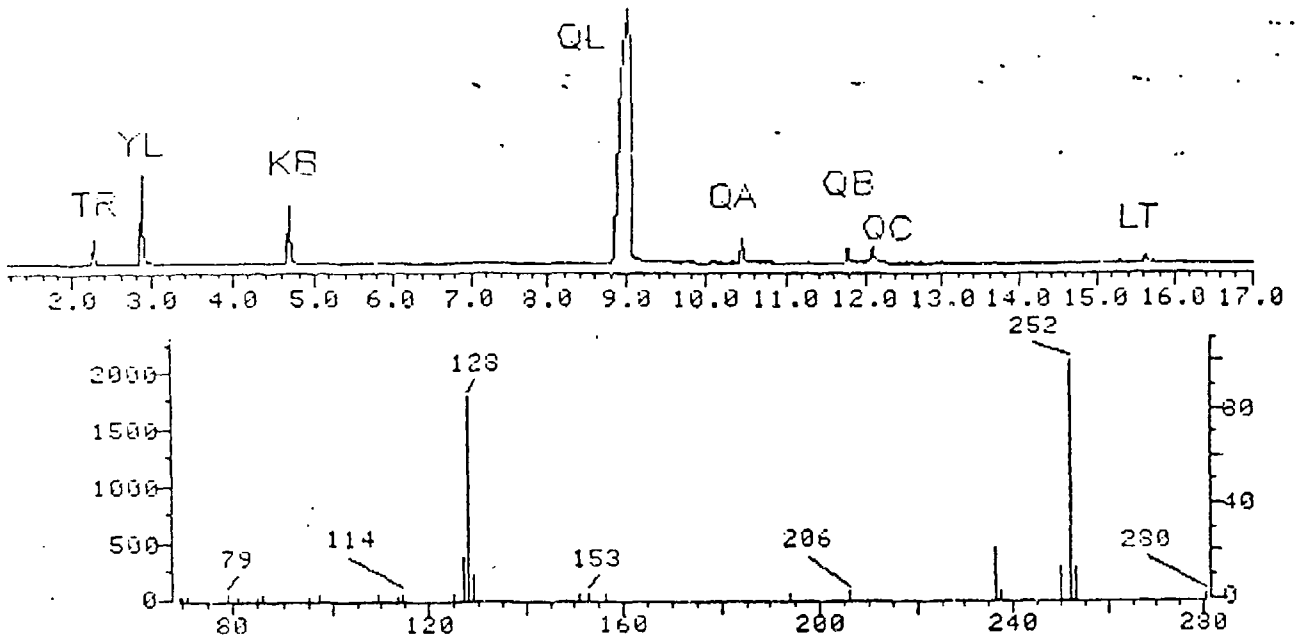
QA O-(2-DiISOPROPYLAMINOETHYL)METHYLPHOSPHINATE MW=207

m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
64.95	1.55	83.05	.03	123.05	.21	145.20	.52	193.20	1.28
69.05	.01	84.05	1.05	128.20	100.00	146.20	3.63	194.05	.65
69.95	.49	85.05	1.00	129.05	11.12	156.20	.63	206.20	6.61
72.05	.36	86.20	2.69	130.05	1.20	164.00	.90	208.20	80.47
79.05	.40	109.15	1.20	137.05	.61	174.15	.69	209.20	8.31
81.05	3.13	114.15	3.05	144.20	.73	192.05	10.58	236.15	1.51

Move cursor; then press carriage return :

Figure 8. MS Spectra for O-(2-Diisopropylaminoethyl) Methylphosphinate (QA)

QL STD CI:Methane



QB

O,O'-ETHYL(2-DIISOPROPYLAMINOETHYL)-METHYLPHOSPHINATE

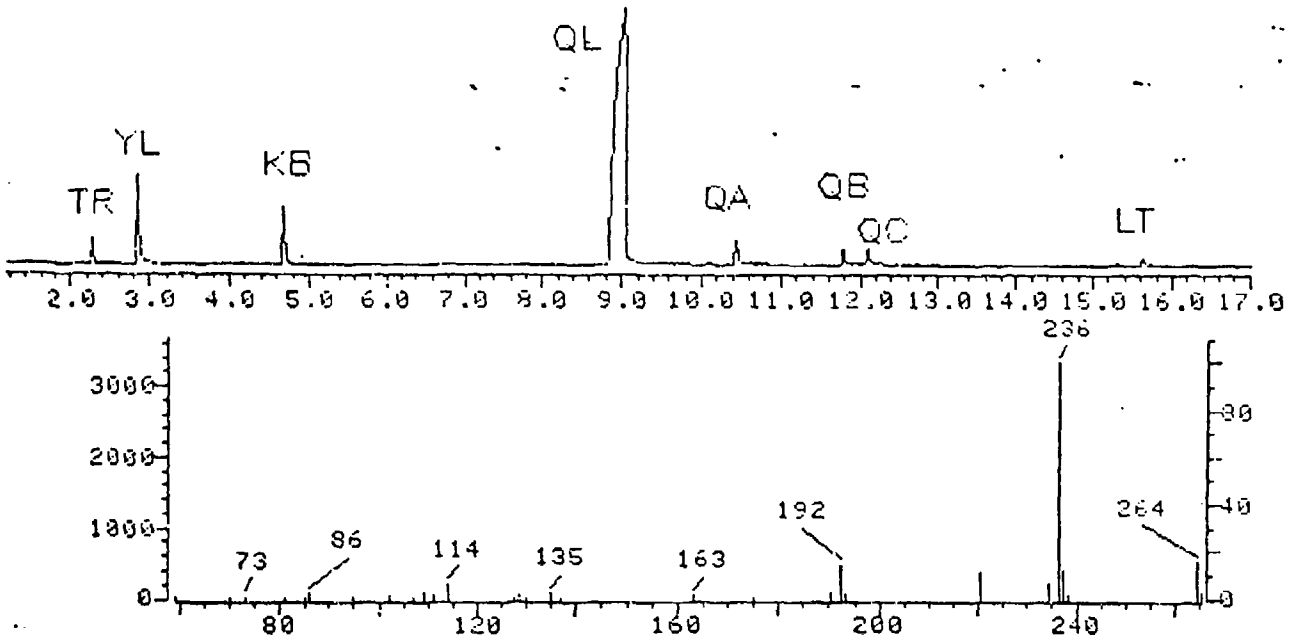
MW=251

m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
69.05	.31	85.05	.93	114.15	1.81	153.05	1.86	237.15	3.05
69.95	.50	86.05	1.81	125.05	1.55	156.20	1.43	250.25	12.67
71.05	.29	95.00	.38	127.20	17.15	194.05	1.19	252.25	100.00
79.05	1.91	97.00	1.26	128.05	84.35	206.20	2.24	253.25	13.12
81.05	.60	109.15	1.14	129.05	9.50	236.15	21.20	280.20	1.52
83.05	.82	113.15	.86	151.05	1.43				

Move cursor; then press carriage return :

Figure 9. MS Spectra for O,O'Ethyl(2-Diisopropylaminoethyl) Methylphosphinate (QB)

QL STD CI:Methane



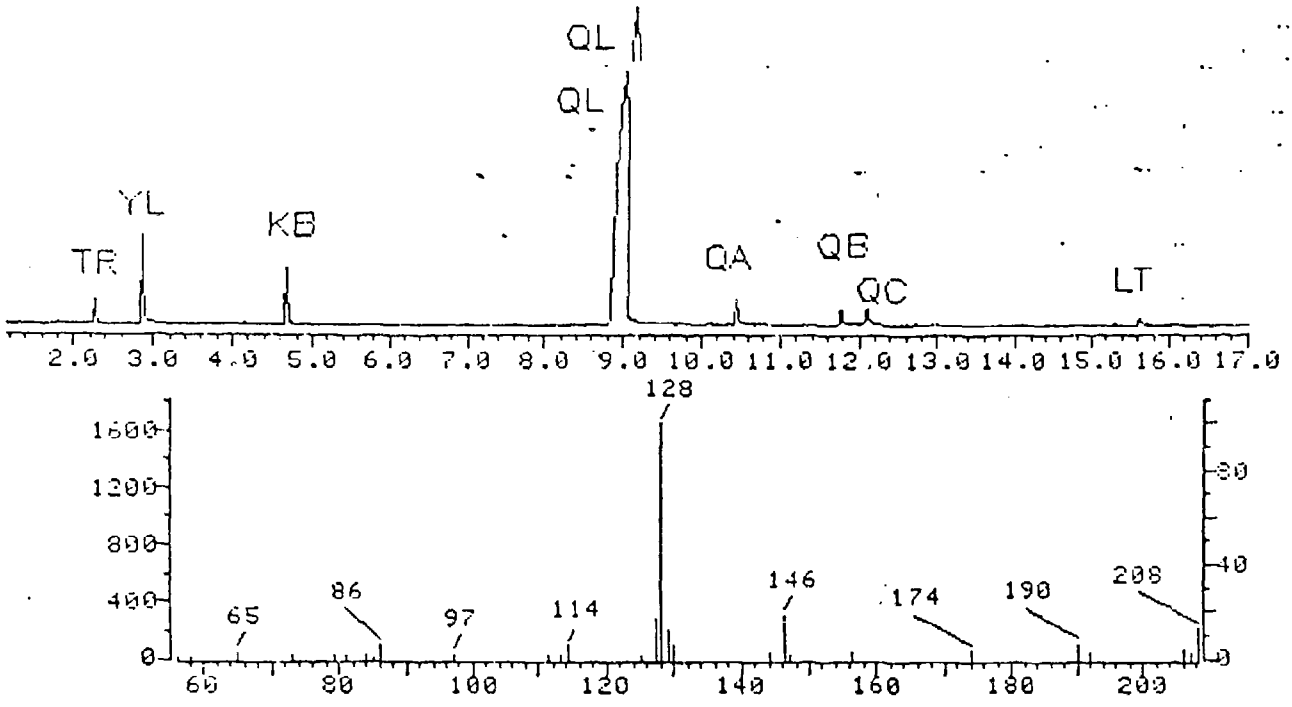
QC O-ETHYL(2-DIISOPROPYLAMINOETHYL)METHYLPHOSPHINATE MW=235

m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
58.95	.09	95.00	.46	127.20	.84	175.00	.51	236.25	100.00
70.05	.07	102.15	1.42	128.20	1.06	190.15	2.83	237.25	11.92
72.95	.66	107.00	.60	130.05	.69	192.05	14.29	238.15	1.26
81.05	.24	109.15	2.11	135.05	2.49	193.05	1.71	264.20	15.89
85.05	.06	111.15	1.29	137.05	.39	220.20	11.11	265.20	2.76
86.05	2.25	114.15	6.13	163.15	1.38	234.15	6.78		

Move cursor; then press carriage return :

Figure 10. MS Spectra for O-Ethyl(2-Diisopropylaminoethyl) Methylphosphinate (QC)

QL STD CI:Methane



LT BIS(2-DIISOPROPYLAMINOETHYL)METHYLPHOSPHONITE MW=334

m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.	m/z	Int.
56.05	.43	84.05	1.78	114.15	5.50	144.05	2.54	190.15	6.10
57.95	.36	85.20	.73	125.05	1.99	146.20	18.74	192.05	2.78
64.95	2.96	86.05	5.68	127.20	17.29	147.05	1.87	206.20	3.32
72.95	1.51	97.00	1.75	128.05	100.00	156.20	2.48	207.20	2.78
79.05	1.12	111.15	1.24	129.20	11.63	174.25	3.20	208.20	12.81
81.05	1.63	113.15	1.63	130.05	5.32				

Move cursor; then press carriage return :

Figure 11. MS Spectra for O,O'-Bis(2-Diisopropylaominoethyl) Methylphosphonite (LT)

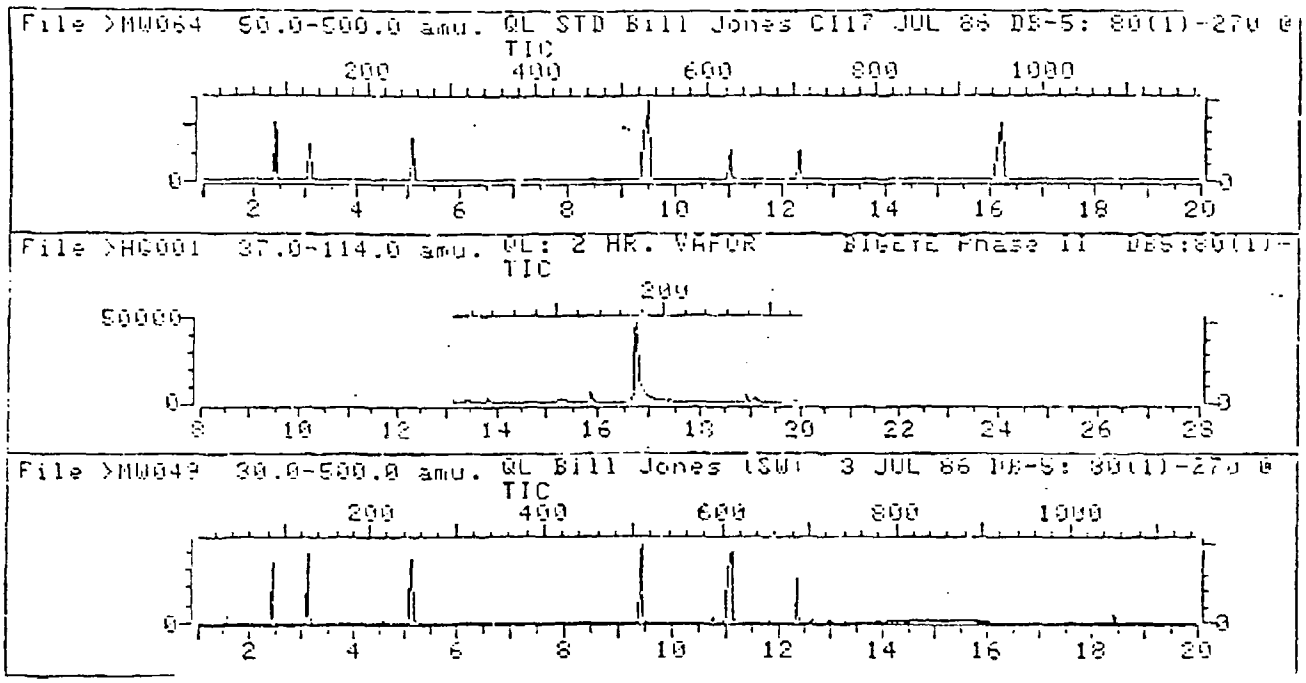


Figure 12. MS Spectra for QL Standard

a. The top spectrum is the elution pattern of a chromatographed QL sample. This pattern appears on all the mass spectral data sheets.

b. The fragmentation pattern appears in the middle spectrum of each data sheet.

c. The tabular values below the graph indicate the mass to charge ratio (m/z) and its intensity (Int.) throughout the entire scan. These spectra should provide valuable reference material for further studies that include QL and the other compounds used in this evaluation.

3.2.2.1 Gas Chromatography

The DB-5 30-m capillary column was programmed from 80 (held for 1 min) to 270 °C at 10 °C/min.

The carrier gas, helium, was maintained at a head pressure of 10 psig, producing a flow of approximately 1 cm^3/min. Injections were made in the split mode with approximately 100:1 ratio.

The compound QL was examined by GC/MS using electron ionization (EI) (70 V) or chemical (methane) ionization (CI). In addition to the QL, seven other compounds were identified.

- CI Mode. The reagent gas was methane, regulated to obtain a source pressure of 1 torr. The source was maintained at 100 °C. Scan range was 50-500 dalton (d).

- EI Mode. The source was maintained at 200 °C. Scan range was 30-500 d.

The quasimolecular ion (M+) was assigned and confirmed by the presence of the $M(C_2H_5)+$ adduct to each of the compounds and their retention times identified using the CI mode. EI spectra were then recorded and identifications made by reference to each of the component's retention times. Samples of QL were generated in the vapor state using an AID Model 250 Diffusion Calibrator. Vapor samples were collected with an 8-in. by 1/4-in. glass tube packed with adsorbent material consisting of glass beads, Tenax-GC, Ambersorb XE-340, and charcoal. The samples were thermally desorbed using an Envirochem Model Unacon 810B concentrator onto a trap, similar to the adsorption tube, at ambient temperature. The trap was thermally desorbed by flash heating (350 °/15 s) onto a second trap, which was an 8-in. tube with a capillary bore packed in a similar fashion to the first trap. The second trap was thermally desorbed (350 °/15s) onto a J&W DB-5 30 m by 0.25 mm capillary chromatographic column that was interfaced directly into the source of a Hewlett Packard (HP) MS, model 5970. The eluting peaks were identified by their EI spectra and retention times.

The GC/MS data were compared to the previously analyzed standard samples using an HP RTE/6 data system. The peak assigned to QL vapor agrees with that assigned to the standard compound analyzed by injection as neat material. The apparent discrepancy in the retention times is due to the 8-min desorption and concentration operation of the Envirochem unit (see MS spectra Figures 4-12).

3.2.3 NMR Methods for QL, TR, TEP, KB, YL, and LT.

Originally, it was proposed to submit samples of QL, TR, TEP, KB, and YL for periodic (monthly analysis) by NMR; however, because of close comparative results of NMR and GC analysis it was decided that such a rigid quality control schedule was not needed. Instead frequent GC analysis would be adequate. The NMR spectrometer used in running these analyses was a Varian XL 200 m/z Super Conducting System; specifications were processed at minimum (Appendix C).

a. The spectrometer had a minimum magnetic field strength of 4.3 tesla and suitable interval on externals field frequency lock.

b. The spectrometer had a resolution of at least 0.5 Hz.

c. The sensitivity of the spectrometer was such that the Carbon-13 sidebands were readily observed at high amplitude.

d. The spectrometer was capable of sweeping from 0 delta to at least a downfield value of 17 delta.

The samples were prepared by placing approximately 0.5 mL of each control material in dry (moisture free) NMR tubes.

The filling procedure was done inside an environmentally controlled humidity chamber at 34% relative humidity (RH). The chamber, which was continuously purged, was zero air at -60 °F dew point.

The characterization spectra of these compounds are included in this report to serve as future reference. Spectra for each compound are included. The mole percent purities reported are representative of actual samples used throughout the study. Tables 8-13 show NMR analyses done in October 1985 and again in August 1986.

Table 8. NMR Analysis for TR

Compound	October 1985	August 1986
TR	94.2 wt %	95.20 wt %
Other	3.43	3.40
pyridine	1.48	1.0
benzene	0.48	0.3
OCH	0.39	0.3

Table 9. NMR Analysis for YL*

Compound	October 1985	August 1986
YL	61.0	82.4
$CH_3P(O)(OR)(OH)$	27.0	1.4
Et OH	6.0	7.3
Other acids and oxides	4.0	4.2
$R_2P(O)(OR)$ type	0.4	1.4
$(RO)_2P(O)H$	1.1	1.4
$(RO)_2P(O)(OH)$ or $(RO)_3P(O)$	0.1	
$(RO)P(O)(OH)H$	0.5	3.4

*A calculated weight percent purity for YL is 59.9%.

Table 10. NMR Analysis for TEP (Aldrich Lot No. 0716PJ)*

Compound	October 1985	August 1986
TEP	95.1	93.9
$(RO)_2P(OR)_1$	0.4	0.4
pyros and phosphonic acids and oxides	0.9	0.5
$(EtO)_2P(O)H$	1.6	2.0
TEPO, $(EtO)_3$ P=O	1.8	2.6
$(EtO)_2P(O)(OH)$	0.1	0.1
TEPPO, $(EtO)_2$ P O P $(OEt)_2$	trace	0.1

*A calculated weight percent purity for TEP is 94.8%.

Table 11. NMR Analysis for KB

Using the $(CH_3)_2$ space region we find:

Compound	October 1985	August 1986 (mole %)
KB	99.2	99.3
Other	0.8	0.7 No other

No other impurities by ^1H NMR.

Table 12. NMR Analysis for QL*

Compound	October 1985	August 1986 (Area %)
QL	28.8	97.3
LT	16.7	0.7
TR	12.7	0.6
$CH_3P(O)(OR)H$	14.9	0.5
$CH_3P(O)(OR')H$	17.4	1.5
$CH_3P(O)(OR)_2$ and $CH_3P(O)(OR)(OH)$	3.9	3.5
$CH_3(O)(OH)H$	4.8	0.7
Others	0.7	0.1

*A calculated weight percent purity for QL is 27.9%.

Table 13. NMR Analysis for LT (Run 3R Hildebrandt)*

Compound	October 1985	August 1986
LT	94.4	93.3
$CH_3P(OR)_2$type	0.3	0.4
$CH_3P(O)(OR)_2$	2.4	3.5
$CH_3P(O)(OR)H$	1.4	1.5
$CH_3P(O)(OR)(OH)$	0.5	0.4
Other	0.9	0.7

*A calculated weight percent purity for LT is 94.3%.

3.3 Test Apparatus.

The test apparatus and calibration unit are shown in Figures 13 and 14. This equipment consisted of a diffusion generator that transmitted candidate vapor through flow tubing into a mixing chamber and then to a three-port glass manifold to permit simultaneous sampling of the vapor stream used to challenge the PA 260 or the MIRAN 80. There were essentially two calibration setups. One system was designed to provide vapor phase concentration of the candidate compounds using air at -60 °F dew point. Vapor concentrations in both setups were changed by either varying the temperature in the diffusion chamber or increasing or decreasing the dilution air.

3.3.1 Diffusion Devices.

The system consisted of a QL vapor generator whose output was mixed with humidified air at select levels between 30 and 80 % RH. QL vapor was generated from a 5-mm id by 4 m long diffusion tube, thermostated in a diffusion tube cell. This diffusion tube was filled with neat QL liquid. The QL vapor emitted by this device was swept by zero air at a -60 °F dew point.

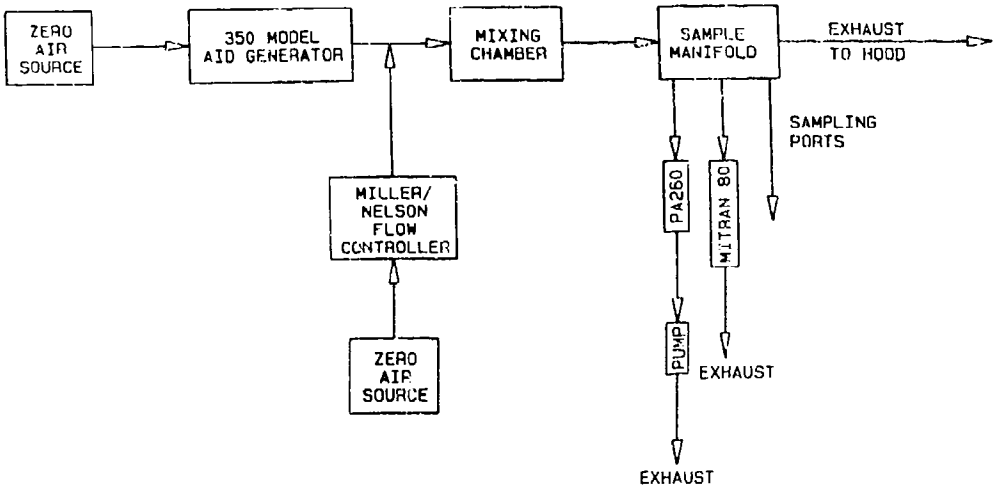


Figure 13. Test Apparatus and Model 350 Calibration Unit

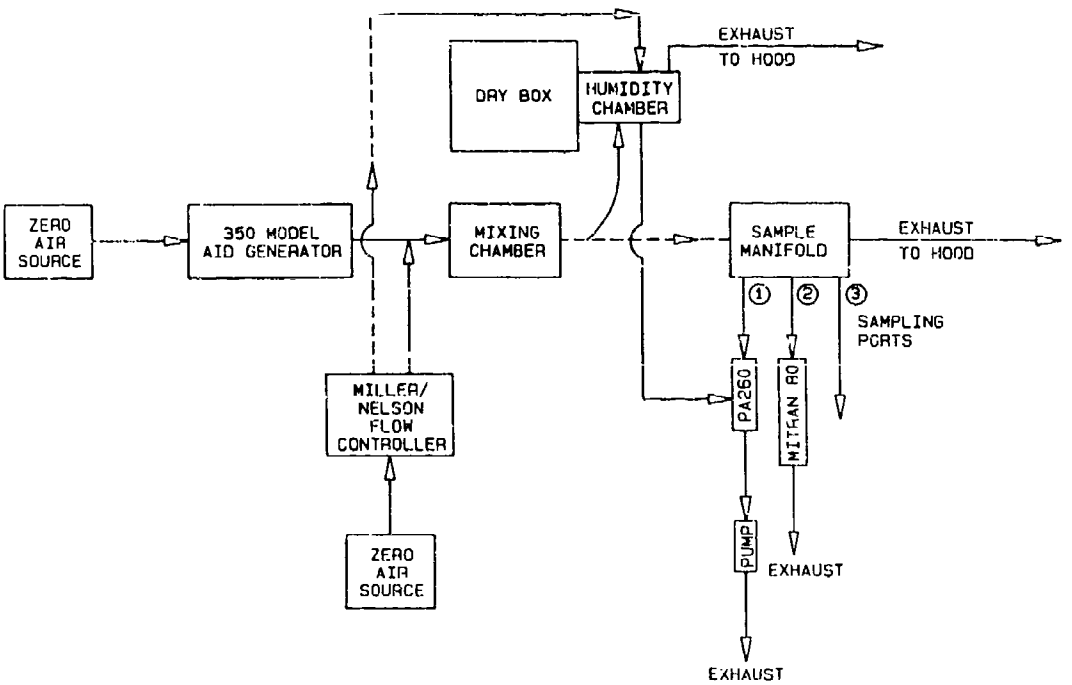


Figure 14. Test Apparatus, Model 350, and Humidity Chamber

A diffusion tube consisted essentially of a small reservoir connected to a length of tubing. The reservoir was filled with the substance of interest in liquid form and the vapor of this substance then diffused out through the tubing at a rate dependent upon the temperature, the vapor pressure, the diffusion coefficient of the diffusing species, and the cross sectional area of the tube. The diffusion rate was determined gravimetrically; however, it may be calculated by the following equation:

$$Q = \frac{DMPA}{LTR} \ln \frac{P}{P-p} \qquad (3)$$

Where:

Q = diffusion rate, D = diffusion coefficient, M = molecular weight of diffusing species, P = pressure in the diffusion cell, A = cross sectional area of diffusion tube, R = gas constant, T = absolute temperature, L = length of diffusion tube, and p = partial pressure (i.e., vapor pressure of the diffusing species).

The diffusion rates of QL, TR, and YL, plotted as decrease in mass versus time in days over 18 days, are included as Figures 15-17. All of the candidate compounds were generated in this manner. Ordinarily, substances with reasonably high vapor pressures of 0.1-0.5 mm of mercury (Hg) would be generated by permeation rather than diffusion. Since diffusion rates are temperature dependent, the reader should note the temperatures at which each compound was generated.

Generation of QL vapor was attempted at 30, 50, and 70 °C. It was possible only at 70 °C to generate QL at 0.1 mg/m^3 using a 5 mm id diffusion tube. To generate larger concentrations, investigators may use more than one tube in the same chamber.

3.3.2 Development of QL Permeation Tubes.

There are two widely used permeable materials that are offered commercially; they are constructed of either fluorinated ethylene Propylene (FEP) or tetrafluoroethylene (TFE Teflon). These permeation tubes [developed by O'Keefe and Ortman at the Environmental Protection Agency (EPA)] provide a gravimetrically prepared standard for calibration of air pollution monitoring such as the PA 260 (Appendix D).

In an attempt to develop a permeation tube to generate a QL gas standard, a permeation tube approximately 10 cm in length constructed of TFE was used. TFE was chosen because of its greater porosity. All attempts to generate QL by this method were unsuccessful. When the absence of weight loss indicated that QL was not permeating the walls of the tubing, further attempts were abandoned.

3.3.3 Reliability and Sensitivity of the PA 260.

The reliability and sensitivity of the PA 260 are well documented. Data are included in reports on the Disposal Protective Ensemble (DPE) program and the Phase I Binary Production Program. The later study was done by Research Directorate. During Phase I, difluoro was

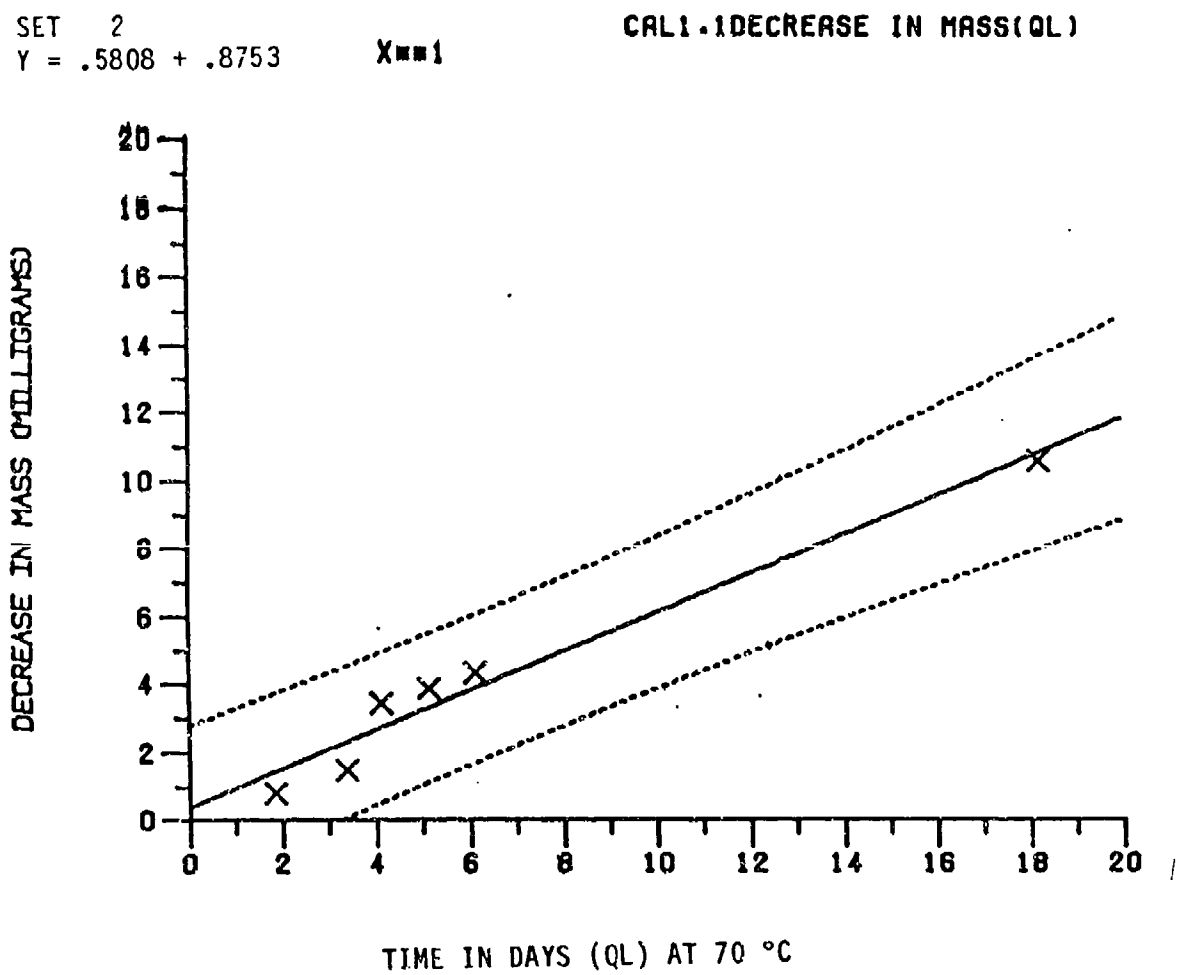


Figure 15. TR Reliability (Calibration)

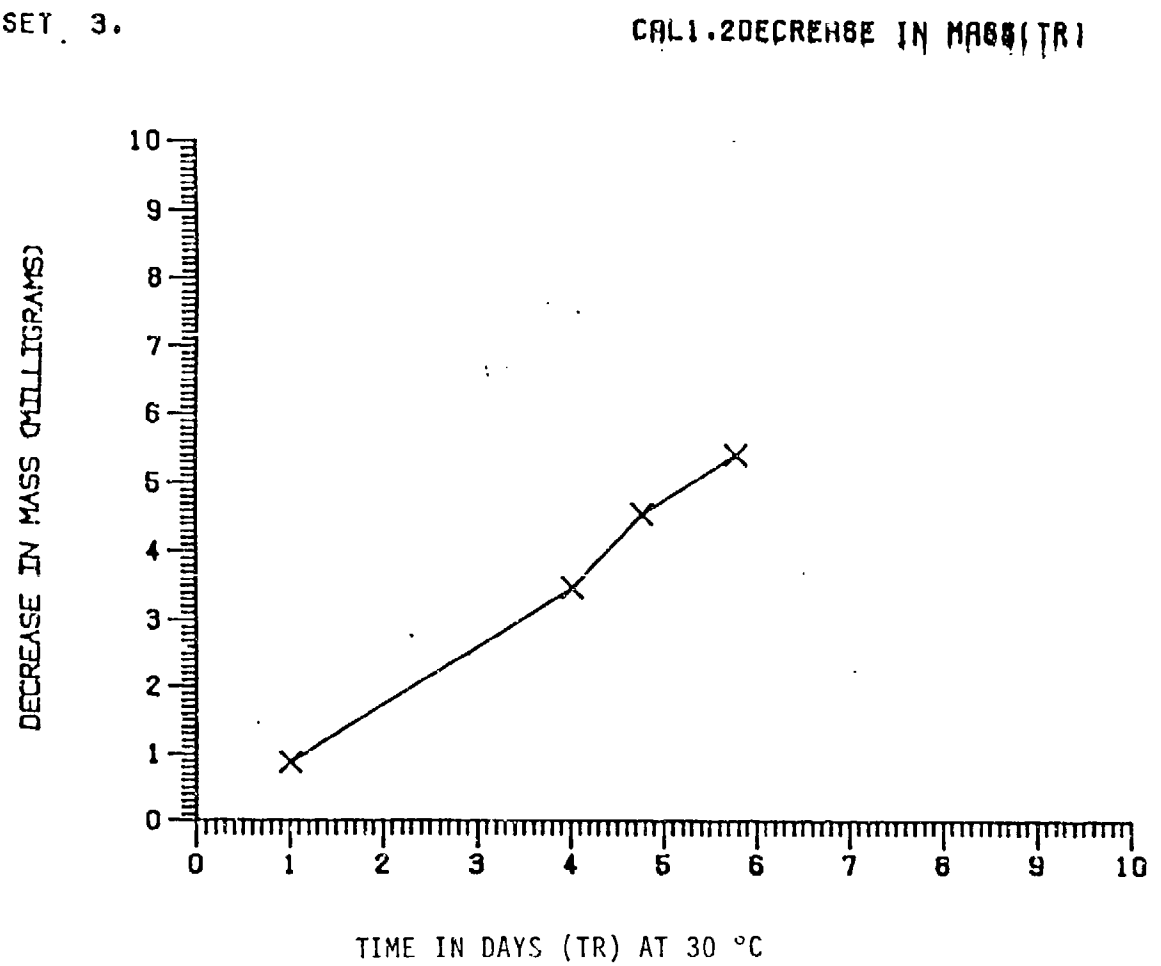


Figure 16. YL Reliability (Calibration)

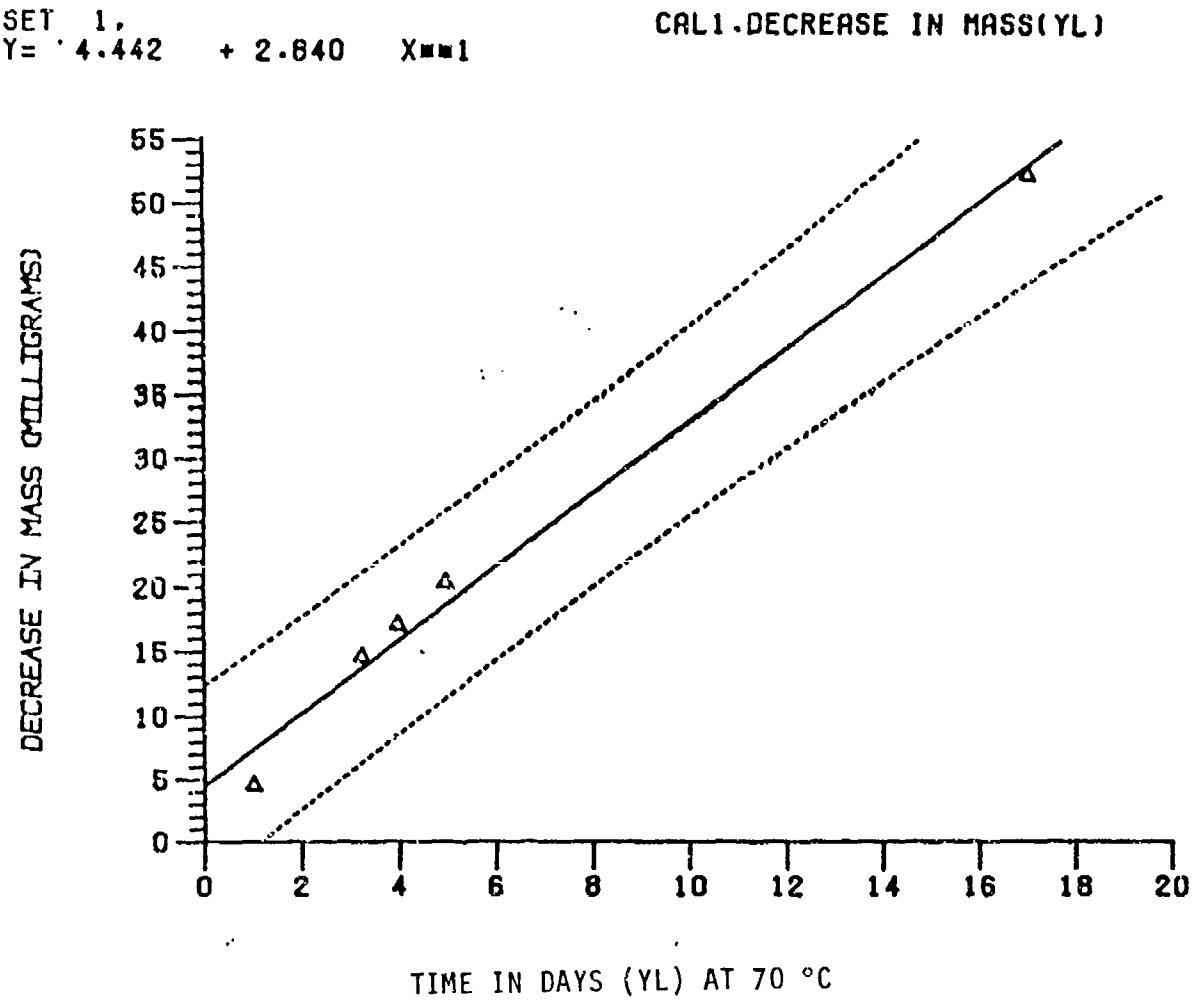


Figure 17. Diffusion Rate Data

determined at 0.002 mg/m^3 with relative standard deviation; as expected, QL and its related products were no exception. The primary concern was the dissemination of these compounds.

Reliability and sensitivity studies began in August 1985. Prior to this date, all attempts to generate QL vapors were futile. After a successful method for dissemination was developed, it required a suitable solvent for a collection medium. Various solvents such as hexane, chloroform, cyclohexane, 2-methylethanol, 2-2-3 trimethylpentane diethyl succinate, and dibutylphthalate were tried without success. Redistillation, drying attempts, and additional solvents were not successful. A suitable collection medium could not be found.

It was decided that these studies would be based on the precision responses of the PA 260 to set concentrations, as determined by weight loss of calibrated diffusion devices (see section 3.4). Table 14 shows the reproducibility of responses of the PA 260 to QL. For example, the calibration data in this table shows a percent relative standard deviation of less than 2%. This includes response values at the parts-per-billion level, which tends to increase standard deviations associated with such measurements. An example of this is the reliability data shown in Table 15 for TR. A rather large standard deviation was found for measurements at 0.006 mg/m^3. This trend is predictable since control of such concentrations is most difficult. The mean response values expressed in the reliability tables were used to create the calibration curves reported in this study. In all cases, the relative standard deviation was less than 2%. Sensitivities were determined for QL, TEP, TR, and YL at 0.22 mg/m^3, 0.006 mg/m^3 , and 0.05 mg/m^3, respectively. The system shows good sensitivity, adequate reliability, and reasonable linearity with one exception--it diverges from linearity at high concentrations. Although this divergence is not critical in terms of total system use, it would be desirable to achieve a linear response over the entire decade range. Table 16 presents the reliability data for YL.

Table 14. QL Reliability Data (Calibration)

Date	Test Duration (hr)	No. of Challenges	Average Challenge Voltage	Conc (mg/m^3)	Rel % SD	Sensitivity Scale
Jul 86	4	7	0.2635	0.022	1.28	$1x10^{-8}$
	4	9	0.3202	0.090	1.24	$1x10^{-7}$
	8	10	0.1358	0.050	1.20	$1x10^{-7}$
	8	11	0.1862	1.049	1.17	$1x10^{-6}$
	4	10	0.4421	1.611	1.23	$1x10^{-6}$

Table 15. TR Reliability Data (Calibration)

Date	Test Duration (hr)	No. of Challenges	Average Challenge Voltage	Conc mg/m^3	Rel % SD	Sensitivity Scale
Sep 86	4	9	.3199	0.006	20.03	$1x10^{-8}$
	4	9	.6883	0.011	4.26	$1x10^{-8}$
	6	9	.1630	0.026	0.54	$1x10^{-7}$
	7	8	.1512	0.246	6.26	$1x10^{-6}$

Table 16. YL Reliability Data (Calibration)

Date	Test Duration (hr)	No. of Challenges	Average Challenge Voltage	Conc mg/m^3	Rel % SD	Sensitivity Scale
30 Jul	6	10	0.1357	0.0516	1.88	$1x10^{-8}$
31 Jul	6	10	0.1092	0.1690	1.93	$1x10^{-7}$
1 Aug	7	10	0.2688	0.2950	1.91	$1x10^{-7}$
4 Aug	6	10	0.4421	1.6110	2.00	$1x10^{-6}$

3.4 Calibration and Analysis.

Calibration of the PA 260 for QL and its related compound is based upon responses to diffusion rates of different sized diffusion tubes. Diffusion rates were determined for QL and YL at 70 °C, using 2-mm and and 0.5-mm diffusion tubes, respectively.

Diffusion rates for these compounds are listed in Table 17. The PA 260 was challenged with various concentrations of QL, TR, and YL; 0.02-1.042 mg/m^3 QL, 0.006-0.246 mg/m^3 TR, and 0.05-1.61 mg/m^3 YL.

Diffusion rates for these compounds were determined by weight loss over time. They were thermostatically housed in model 350 and 580-3C standards generators. Both generators operate on the same principle (see Appendix E). They require large quantities of dilution air in order to reach TLVs. For example, greater than 30 L of dilution air per minute were required to attain a vapor concentration of 0.006 mg/m^3 for TR. The maximum dilution capabilities of the Model 350 AID and the Kintek 580-3C generators are approximately 20 L. To attain the quantity of dilution air needed, the affluent from the generator was mixed with an external source of dilution air at a glass tee, in this case, provided by a Miller Nelson flow controller. This unit is capable of delivering up to 100 L/min that is sent to a gas vortex mixing chamber and then to an open three port sampling manifold that exhausts excess flows into the fume hood. This was shown schematically in Figures 13 and 14.

Table 17. Diffusion Rate Data

Compound	Differential Wt Loss (mg)	Time (days)	Diffusion Rate ng/min	Temp °C
QL	0.8	1.84	301.9	70
	0.67	3.37	303.0	70
	1.94	4.11	439.3	70
	0.45	5.11	314.6	70
	0.46	6.10	321.7	70
	6.27	18.21	359.7	70
TR	3.47	4.03	597.73	30
	1.09	4.78	590.9	30
	0.86	5.78	598.4	30
YL	4.46	1.0	3099.8	70
	14.48	3.25	3089.4	70
	2.44	3.99	2284.6	70
	3.26	4.99	2273.4	70
	32.12	17.10	2372.4	70

Because the manifold had three sampling ports, both the MIRAN and the PA 260 were challenged at the same time for any given candidate compound. Challenge concentrations of QL, TR, YL, and TEP were obtained through a 3-m length of 1/8-in. od Teflon line. Typical concentrations during calibrations for QL were listed in Table 14. A lower limit for QL detection was 0.022 mg/m^3 on the 1×10^{-8} ampere output scale and approximately 1.042 mg/m^3 on the 1×10^{-6} scale. The resulting QL calibration curve is seen in Figures 18 and 19. This is a log-log plot. The PA 260 was zeroed and then challenged with 0.022 mg/m^3 of QL vapor. This gave a voltage output of 0.2635 volts, equivalent to 0.26×10^{-8} net current in amperes. Calibration data for QL, TR, and YL were listed in Tables 14-16. Calibration plots for QL, TR, YL, and TEP are found in Figures 18-23.

This net current 2.6×10^{-8} represents a calibration point at 10-7 and 10-6 representing three decreases of response (see Appendix A). The current output (or percent chart) was plotted as concentration for each range on log-log paper. These curves represent the calibration output of the analyzer for each range. If percent of chart is plotted, then the graph shown in Figure 24 should be used to convert the net amperes, where 1×10^{-9} amps equals 0% of chart, 20% of chart equals 1×10^{-8} amps, 40% of chart equals 1×10^{-7} amps, 60% of chart equals 1×10^{-6} amps, 80% of chart equals 1×10^{-5} amps, and 100% of scale is 1×10^{-4} amps.

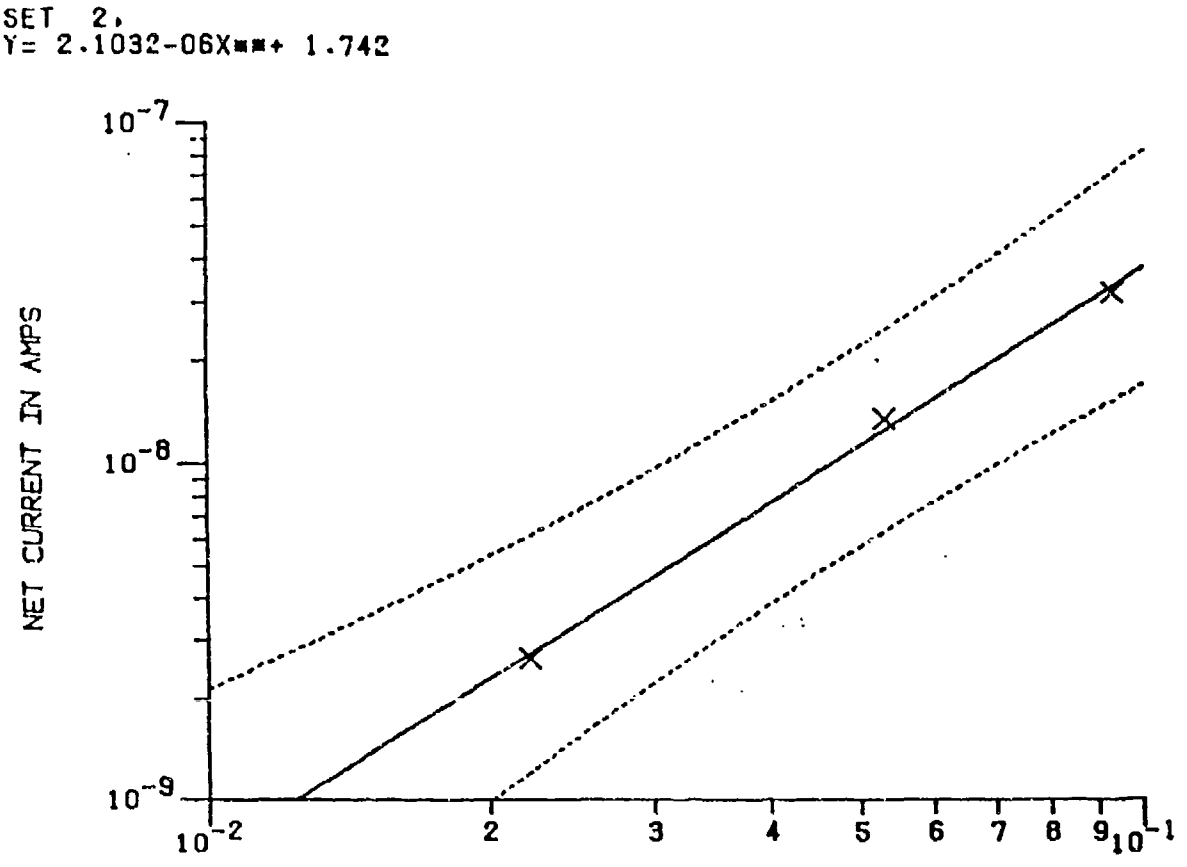


Figure 18. Calibration of PA 260 with QL (with 95% Confidence Lines)

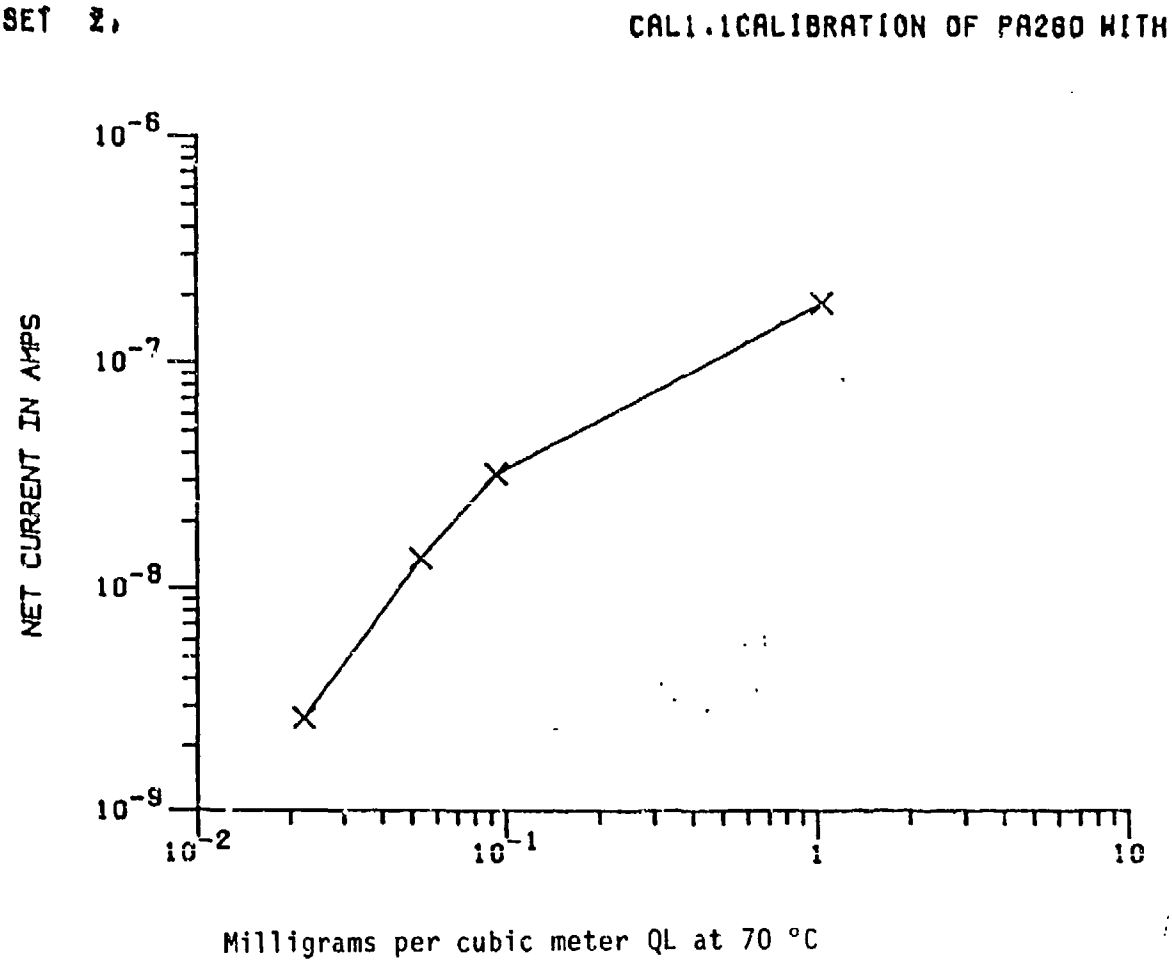


Figure 19. Calibration of PA 260 with QL

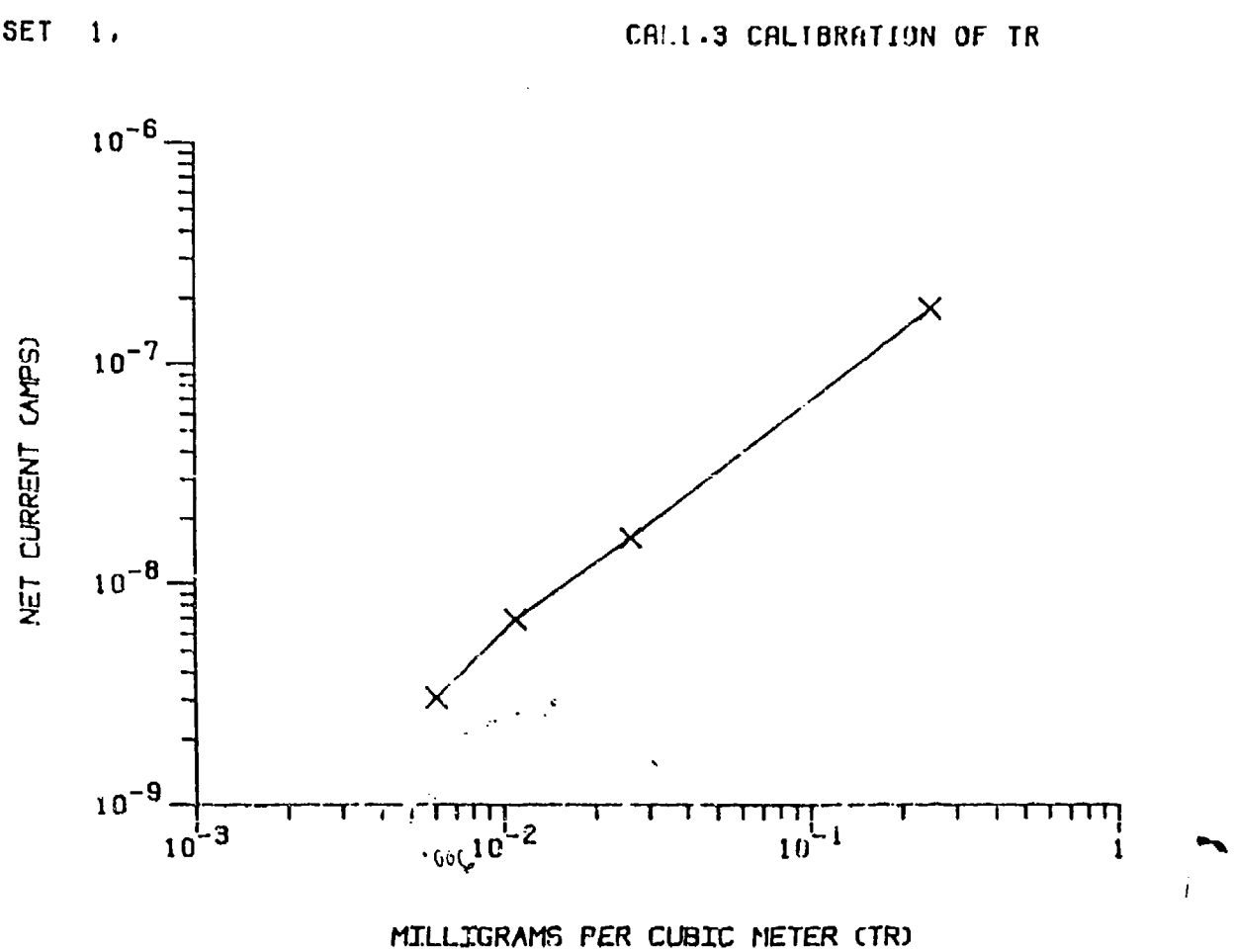


Figure 20. Calibration of TR

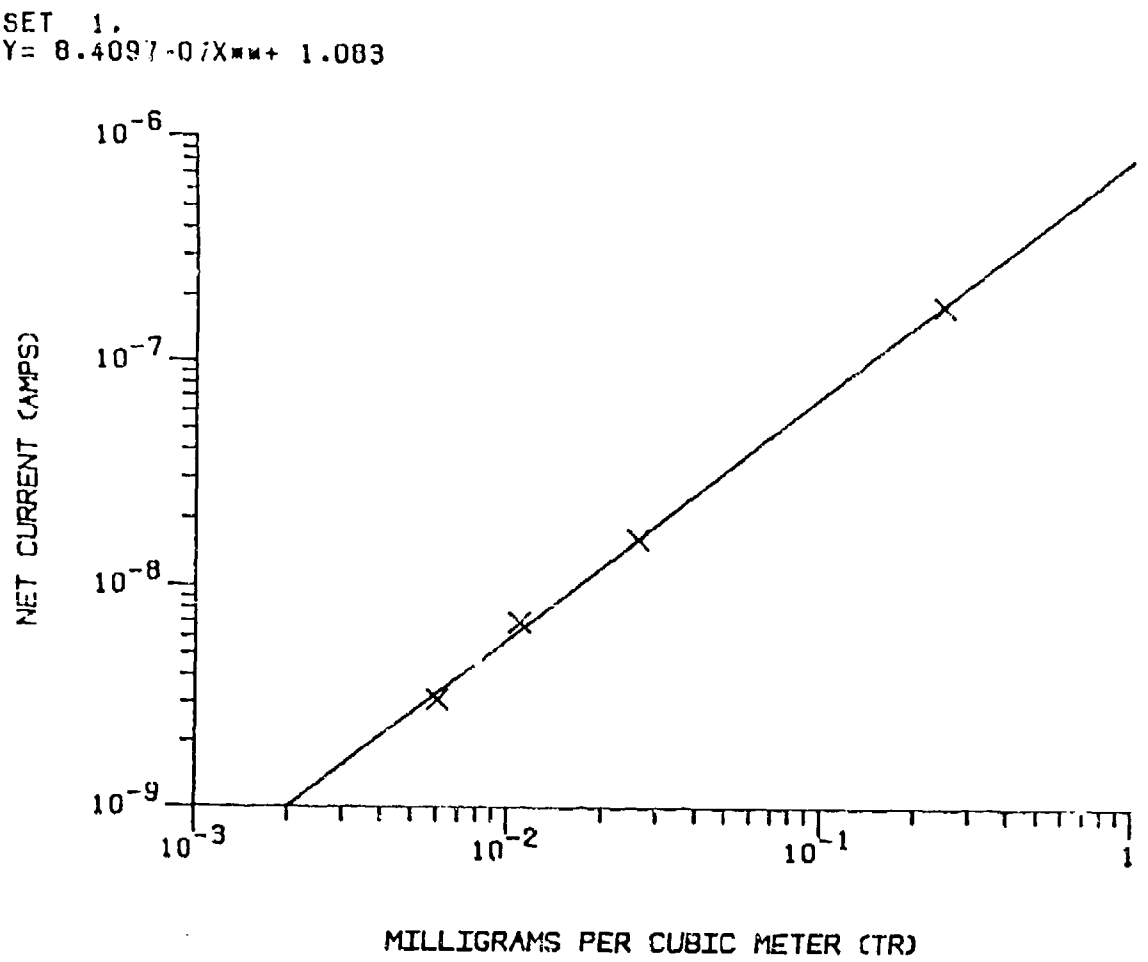


Figure 21. Calibration of TR (Curve Extended to X-Axis)

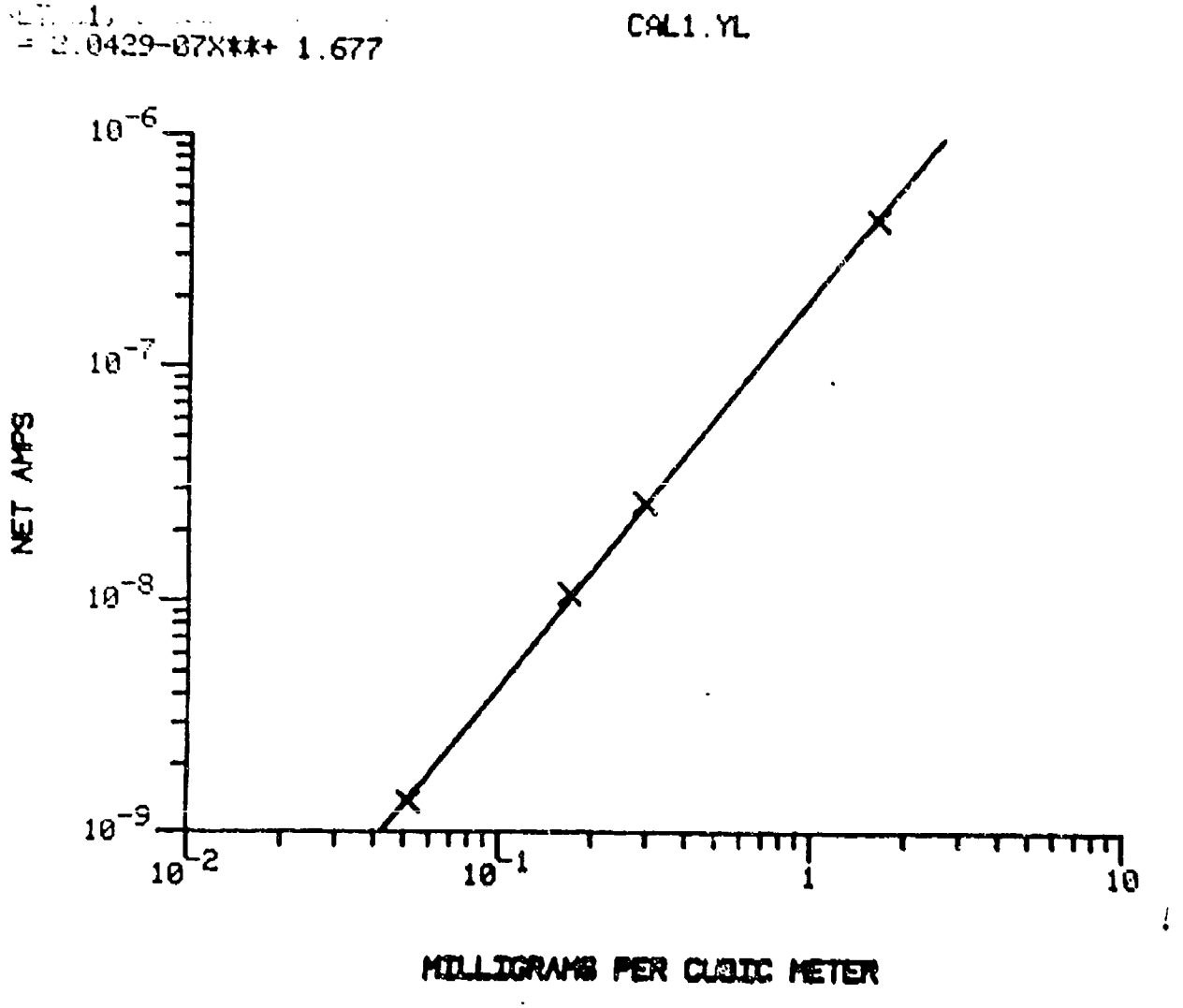


Figure 22. Calibration of YL

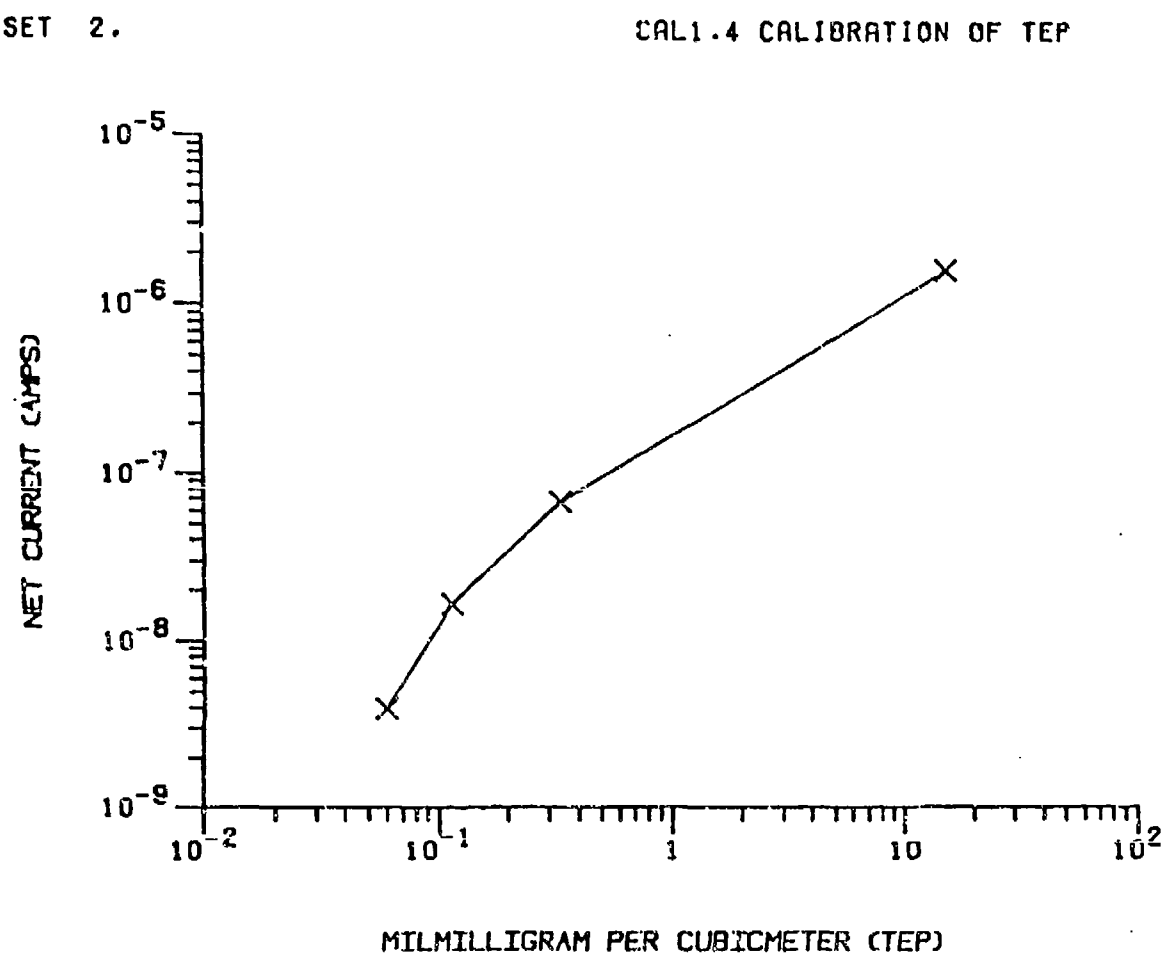


Figure 23. Calibration of TEP

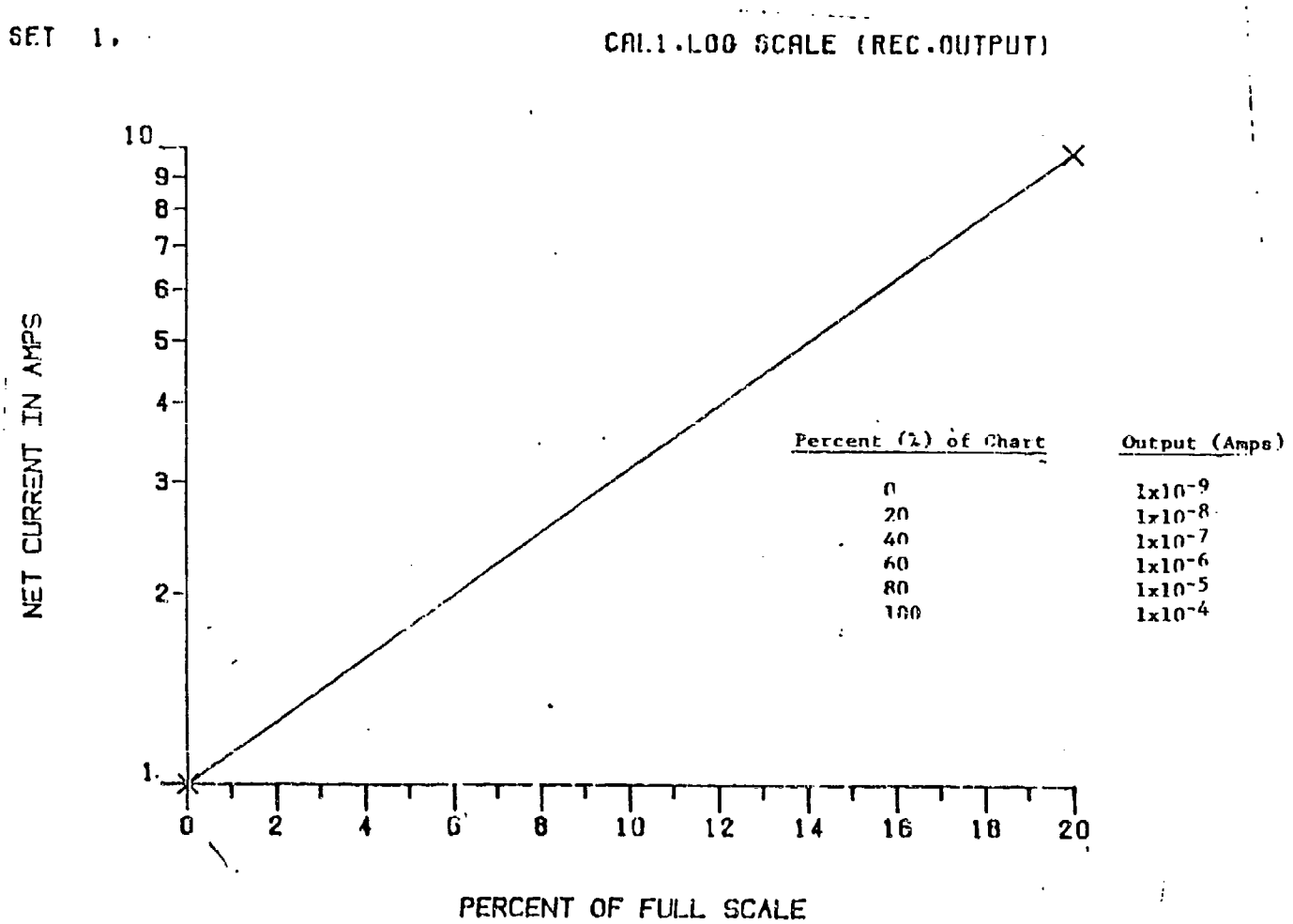


Figure 24. Log Scale (Recorder Output)

Table 18. Humidity Study (32.2% Relative Humidity)

TEST DURATION.....4.0 (Hrs)

	HUMIDITY (TEST)			AMBIENT (TEST)	
CONC (mg/m^3)	RISE TIME (mins)	RESPONSE (Volts)	MEAN RESPONSE ± S.D.	RESPONSE (Volts)	MEAN RESPONSE ± S.D.
	>5.0 min	0.3101		V=0.2910	
		0.3122		V=0.2953	
		0.3200		V=0.2991	
		0.3201		V=0.3000	
		0.3220		V=0.3088	
		0.3254		V=0.2998	m=.2990±.006
		0.3300			% Rel. S.D. = 1.98
		0.3301			
		0.3300			
		0.3310	.3231±.008		
			% Rel. S.D. = 2.35		

TEST DURATION.....6.0 (Hrs)

	>7?.0 min	0.1178		V=0.1011	
		0.1162		V=0.1054	
		0.1182		V=0.1034	
		0.1201		V=0.1026	
		0.1203		V=0.1088	
		0.1201		V=0.1183	
		0.1201		V=0.1154	
		0.1204		V=0.1101	
		0.1210		V=0.1062	
		0.1231	.1197±.002	V=0.1100	.1081±.006
			% Rel. S.D. = 1.59		% Rel S.D. = 5.10

Table 19. Humidity Study (54.2% Relative Humidity)

TEST DURATION.....2.0 (Hrs)

CONC (mg/m^3)	HUMIDITY (TEST) RISE TIME (mins)	RESPONSE (Volts)	MEAN RESPONSE ± S.D.	AMBIENT (TEST) RESPONSE (Volts)	MEAN RESPONSE ± S.D.
	>75.0	0.3500		V=0.2872	
		0.3405		V=0.2875	
		0.3201		V=0.2901	
		0.3110		V=0.2952	
		0.3034		V=0.2888	
		0.2946		V=0.3001	
		0.2854		V=0.3031	
		0.2800		V=0.3041	
		0.2757		V=0.3038	
		0.2724	.3033± .027	V=0.3051	.2899± .0225
			% Rel. S.D. = 8.9		% Rel. S.D. = 7.76

TEST DURATION .....7.0 (Hrs)

	>75.0	0.2260		V=0.1896	
		0.2210		V=0.1921	
		0.2203		V=0.1962	
		0.2210		V=0.1996	
		0.2200		V=0.2010	
		0.2203		V=0.2038	
		0.2204		V=0.2086	
		0.2201		V=0.2101	
		0.2208		V=0.2100	
		0.2804	.2210± .002	V=0.2105	.2022± .008
			% Rel. S.D. = 0.8		% Rel. S.D. = 3.8

Table 20. Humidity Study (70.3% Relative Humidity)

DURATION OF TEST .....4.0 (Hrs)

CONC (mg/m^3)	RISE TIME (mins)	HUMIDITY (TEST) RESPONSE (Volts)	MEAN RESPONSE ± S.D.	AMBIENT (TEST) RESPONSE (Volts)	MEAN RESPONSE ± S.D.
	>4.0	0.2173		V=0.1891	
		0.2162		V=0.1900	
		0.2178		V=0.1903	
		0.2169		V=0.1910	
		0.2175		V=0.1996	
		0.2178		V=0.1998	
		0.2175		V=0.2001	
		0.2178		V=0.2001	
		0.2176		V=0.2042	
		0.2182	.2174± .0006	V=0.2051	.1969± .006
			% Rel. S.D. = 0.2		% Rel. S.D. = 3.13

DURATION OF TEST.....3.0 (Hrs)

		0.2201		V=0.1924	
		0.2301		V=0.1956	
		0.2282		V=0.1988	
		0.2201		V=0.1991	
		0.2221		V=0.2001	
		0.2206		V=0.2021	
		0.2212		V=0.2032	
		0.2204		V=0.2068	
		0.2200		V=0.2081	
		0.2201	.2229± .004	V=0.2101	.2016± .006
			% Rel. S.D. = 1.69		% Rel. S.D. = 2.77

TEP, YL, and TR response calibrations were accomplished in the same manner as QL. These curves are represented in Figures 20-23.

3.5 Quality Assurance Program of QL Storage Samples.

Analysis of QL, KB, TR, YL, TEP, and LT by capillary GC and NMR was done at the beginning of this evaluation and periodically thereafter to ensure that the program stock materials did not deteriorate to unusable levels. All stock materials were received in amber colored bottles except for QL, which was received in a clear glass stoppered bottle. All candidate sample containers were sealed with paraffin and stored in a fume hood.

The analyses performed using GC and NMR are shown in Table 4. It was shown in the beginning of the study that NMR gave comparable results to GC; therefore, back-up analyses with NMR were not required to verify stock purities.

All GC analyses were run in triplicates using the same chromatographic conditions (see Appendix F). It should be noted again that the QL sample that showed a purity of 27.9 wt % was not used during the evaluation but was used to determine the breakdown Products of QL. The QL sample that assayed at 95.87% by GC was used as reference stock material.

Additionally, it was proposed during the early stages of this program that QL, KB, TR, TEP, and LT be ampouled and stored for the duration of the program. The purpose was to have available standards of each of the components.

3.6 Humidity Studies.

To study the effects of humidity on QL in areas such as the state of Arkansas, it was necessary to simulate as closely as Possible the state environmental factors in the laboratory. Climatic conditions in this area are characterized by long periods of very high humidity. Because of this and the fact that some of the area monitors (PA 260s) may be situated outside of the enclosed plant environment, it was vital that humidity studies be done to determine what, if any, effects this would have on the PA 260's responses.

It was decided that the PA 260 data base would include humidity studies at 30, 50, and 70% RH. Our purpose was to cover as wide a range as possible of humidity conditions and then monitor PA 260 responses.

To perform these studies two major pieces of equipment were purchased: (1) an environmental chamber consisting of two separate compartments permiting humidity studies to be done in one while maintaining a dry environment for storage transfer and other moisture free operations in the other and (2) a Miller-Nelson humidity controller capable of delivering 100 L/min of air at a precise humidity.

For the humidity test, the calibration assembly was modified by the addition of the humidity controller and environmental chamber The modified assembly is shown schematically in Figure 14. The effluent from the diffusion generator was directed to the reaction compartment of the environmental chamber, mixed with humidified air, and sampled at yet another port by the PA 260. To avoid a dilution effect, the humidified air was introduced into the chamber at the same rate it was being sampled by the PA 260. Tables 18-20 contain data from experiments that were run at 30, 50, and 70% RH. The data clearly indicate that there is very little net change in PA 260 responses regardless of humidity conditions. These results are not totally unexpected. As might be expected, the hydrolysis of QL is very rapid with the expected production of hydrolysis products such as KB and YL. This conclusion is based upon GC/MS analysis of QL to which trace amounts of water were introduced. Results revealed that when 0.01 mole % of water was added, the QL was quantitatively converted to YL and KB. Additionally, there are other competing reactions that are occurring such as the primary disproportionation products TR and LT. When taking these into consideration and the fact that the PA 260 monitor is a generic detector, no net difference in response is expected. These findings should be an asset, in that, regardless of whether the QL remains intact or not, the detection of its breakdown products are readily accomplished with the PA 260.

3.7 Interference Study.

Questions were raised about the PA 260 and its specificity to compounds containing phosphorus and to its susceptibility to select interferents that do not contain phosphorus. There are many documented experiences with the PA 260 that prove its worthiness in terms of performance and reliability. It is expected that in this proposed plant or any plant environment, interferences may be present that would cause false alarms. This includes both in-plant environments and the surrounding community. To preclude this potential for false positives, a list of possible interferences was generated by Munitions Directorate with the request that the PA 260 be challenged with these potential interferents. Table 21 shows a list of these compounds as traceable standards. The PA 260 was challenged with these components at various concentration levels.

Table 21. PA 260 INTERFERENCES TESTED

Challenge Material	Concentration	Response
Freon 12*	224 ppm	Negative
Freon 113*	Neat	Positive
CO_2*	503 ppm	Negative
HF*	560 ppm	Negative
Cl_2	262 ppm	Negative
CO	149 ppm	Positive
Smoke (cigarette)	Neat	Positive

Table 21. PA 260 Interferences Tested (Continued)

NH_3*	511 ppm	Negative
P2O5		Positive
DC	Neat	Positive
HCl	6 Normal	Negative
Caustic	Neat	Negative
Mineral Oil	Neat	Negative
Ink	Neat	Negative
Helium	Neat	Negative

*Calibrated gas mixtures obtained from Matheson Gas Products Company, East Rutherford, NJ.

These gas-fed standards were introduced into the PA 260 through a three-port glass manifold. This was accomplished by releasing a controlled flow of each of the components at 1 L/min (see Figure 13). The PA 260 was operated in its most sensitive mode (see Appendix A). At these settings the PA 260 is capable of detecting 0.5 ppb of phosphorus containing compounds. This was established in Phase I of the Binary Production Program. The analyzer was challenged for 15 min or until certain compounds gave a negative response. A negative response was characterized by deflection of the recorder pen below the baseline. The negative response is believed to be due to a "quenching effect" of the hydrogen rich flame that exists in the burner block of the PA 260.

Table 22 is a list of the compounds most likely to be present in a plant environment. Challenge concentrations were established by using an order of magnitude of 1,000 times greater than the established detection limit. For instances, where traceable standards were not available, the components were sampled directly from the containers or cylinders they were shipped in upon purchase.

Table 22. PA 260 Summary of Potential Interferences

1.	DF
2.	HF
3.	DC
4.	Caustic
5.	HCl
6.	Freon-22
7.	Mineral Oil
8.	1,1,1 Trichloroethane
9.	Xylene base paints
10.	P2O5
11.	Ink
12.	Helium
13.	Pyropolyphosphate (water treatment chemical approximate 1 ppm)
14.	Expoxy carbon-filled resistant treatment

For example, the PA 260 can readily detect phosphorus compounds in the parts-per-billion range. These components were introduced as parts-per-million to parts-per-thousand concentration range.

It can readily be seen that the PA 260 will respond to cigarette smoke, Freon 113, and certain other compounds. It is suggested that these observations be considered when placing the monitors throughout the plant area.

4. MIRAN 80/980 EVALUATION STUDIES

4.1 Characterization of MIRAN 80.

Evaluation of the MIRAN 80 indicates that the unit is suitable for the detection of KB and YL. Concentration ranges of interest are from the parts-per-billion to the parts-per-million . The MIRAN performed well in the 0.5-10 ppm range for all components tested. Minimum detectable limits (MDL) for the two components was established. The MDL for KB is 0.52 ppm or 0.00306 mg/m^3 and for YL is 0.425 ppm or 0.0018 $mg/^3$ at 30 °C.

Currently, the MIRAN is the only unit evaluated for the specific detection of KB. This section presents the instrumentation, calibration method, concentration determination, Bigeye Bomb (BLU-80/B) shipping container evaluation, and the tabulated graphic data.

4.2 Instrumentation.

Equipment used in the study were as follows:

4.2.1 Wilks Model 80 MIRAN.

A quantitative analysis system combining a high performance single beam infrared spectrometer with a programmable microcomputer system. This unit accepts multi-component liquids, solids, or gaseous samples directly without the necessity of vaporizing or dissolving and separating them into their individual components. The MIRAN 80 (and the MIRAN 980) provide the following capabilities:

a. Measurement of up to 18 separate wavelengths in less than 2 min. The time interval between sets of measurements can be varied from 7 s to 30 min.

b. Signal averaging measurements (256) are made at each wavelength over a 1-180 s interval and averaged to enhance the signal to noise ratio and thereby improve precision.

c. There is quantitation of as many as 11 components with one reference wavelength, compensation for interferences and an absorbance repeatability within the noise level.

d. Keyboard entry of instrument settings and factors for data manipulation. Changing instrumental conditions for a new analysis is rapid (i.e., less than 10 min) to set up a five-component liquid analysis.

e. Print out of memory parameters such as wavelengths, standard factors in data matrix, gain settings, etc.

f. Short section scanning of the spectrum automatically, with printouts of absorbance as a function of wavelength.

g. Data printout including absorbance for each wavelength and concentration for each component.

h. Digital display showing keyboard entry and display of wavelength during the analysis routine.

i. Compatibility with all Wilks standard liquid, gas, and solid sampling devices. The single beam variable filter spectrometer is capable of scanning the infrared spectral range between 2.5 and 14.5 μm The instrument is equipped with a gas cell, having a pathlength variable between 0.75 and 20.25 m. The variable pathlength gas cell has a 5.6 L capacity, is vacuum-tight to 10-5 torr, and pressurizable to 100 kPa (10 atmospheres). The internal optics are gold plated, and the inside of the cell is polytetrafluoroethylene coated to resist sample absorption and corrosion.

NOTE: Unlike the MIRAN 80, the 980 has several other capabilities:

(1) P-Matrix calculation that allows concentration reporting without the use of an external computer.

(2) Micro tape recorder designed to store the 980's calibration parameters.

(3) Intra diagnostic test program that prevents instrument operation if anything electronic or mechanical is faulty.

4.2.2 SpanLab Model 580-3C Vapor Generator.

The KIN TEK vapor generator provides the following capabilities (fully described in Appendix D):

a. The SpanLab 580-3C contains three independently controlled diffusion/permeation units interconnected by inert (Teflon) solenoid valves. Physically, the system is mounted in two interconnected drawers housed in a 24-in wide instrument cabinet. The lower drawer contains the Permeation units and all operating controls. The upper drawer houses an electronic mass flow measuring unit for dilution flow measurements. The meter unit is manually multiplexed to provide measurement of all flows with a single meter unit.

b. A flow diagram of the 580-3C is presented in Appendix E and Figure 25. The dilution gas source enters through the rear of the

instrument and is pressure regulated to approximately 20 psig. This regulated pressure is applied to a gas distribution manifold that feeds four output pressures to the flow measure drawer. One output is provided for multicomponent (sum) dilution flow, and each permeation unit has an output. In the flow drawer, each dilution source is routed either directly back to its respective permeation unit or through the mass flowmeter and thenback to its permeation unit. In the permeation drawer, each dilution flow divides into two paths. The main flow feeds the dilution flow regulator. The dilution flow regulator adjusts and maintains a steady flow of 0.025-2.5 L/min. The other portion of the flow passes through a three-way solenoid valve and feeds the oven flow regulator. The oven flow regulator adjusts and maintains a steady flow of 0.02-0.2 L/min over the permeation source. This flow passes through a preheated tube in the oven and joins with the permeate flow of the component to form a primary mixture that is routed through a pair of Teflon solenoid valves to either join the main dilution flow for that unit, the sum flow, or be discarded to the vent. When the oven flow and permeate are routed to the sum flow, the oven flow is taken from the sum flow, so the measured flow for either mixture is always the actual total flow (this is diagramed in Figure 25).

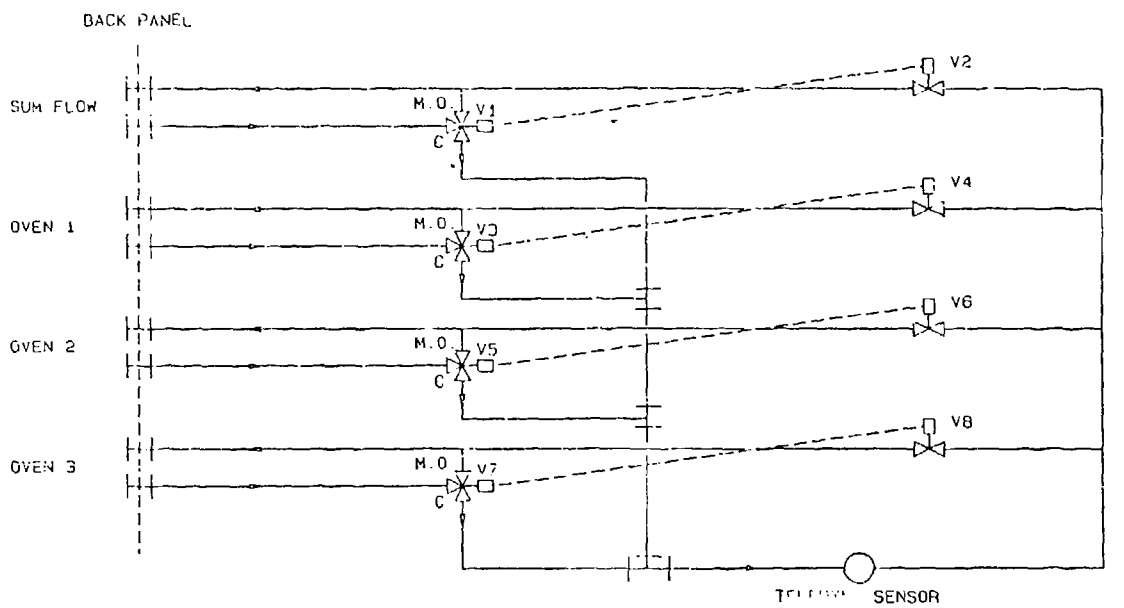


Figure 25. Flow Diagram of SpanLab Gas Generator

c. To provide the capability of filing series 57 gas fed sources with component gas, each unit has an all stainless flow path with a precision pressure regulator and guage, a preheated tube in the oven, a needle valve, and shutoff valve for flow control. The component gases and each mixture enter and exit through the front panel of the permeation drawer.

d. The preparation of precise low concentration gas blends using the permeation method requires accurate control of the permeation source temperature, precise control and accurate measurement of the dilution flow rate and component gas pressure, and careful selection of materials in contact with the low concentration blend. The SpanLab 580-3C is designed to provide the high standards of precision and accuracy required in a precise laboratory gas standards generator.

e. Each permeation unit has a high thermal mass heating system. Temperature is controlled at three preselected points by precision mercury-in-glass thermostats coupled to the heating system by a zero-switching, solid state power switch. This simple system is a key feature of the instrument. Temperature settings have a fixed known accuracy with minimal drift and are traceable to the National Bureau of Standards.

f. Figure 26 (and the figure in Appendix E) illustrate the permeation tube assembly and glass bottle into which diffusion tubes containing components of interest are placed. This modification was made to generate gas samples.

4.2.3 Alternatives.

As an alternate means of determining the concentration levels of vapors created by the SpanLab 580-3C, the following GC units were used to analyze the components before filling diffusion tubes. Hewlett Packard 5830A

equipped with a Thermionic detector and a Carbopack +0.5 KOH column for the KB component.

Hewlett Packard 5840 equipped with a Flame Photometric Detector (FPD) and a DB5 Megabore column (0.53 mm od) for the YL component.

Varian 6000 equipped with a thermionic flame ionization detector (FID). The Megabore DB-5 column is used for the FPD and a D-6 capillary column (0.25 mm od) for the FID. Again these were used as confirmation tools.

These systems were to provide a three-way check for expected concentration levels of bubbler samples pulled and purity analysis. Note that in all the experiments described, an adequate collection medium could not be established. Therefore, the three-way check for KB and QL was not feasible. A list of solvents examined for collecting KB, QL, and YL will be provided upon request.

4.3 Calibration (Techniques) Methods.

Two methods were used to calibrate the MIRAN 80. These methods are the isolated loop process for liquid samples and a continuous flow method for gas phase samples (Appendix G).

4.3.1 Isolated Liquid Injection Method.

The isolated liquid injection method is the manufacturer's method of calibrating this instrument. Equipment in addition to the MIRAN are:

a. Teflon circulating (vacuum) pump

b. Stainless steel tubing (1/4 in. id)

c. Assorted swageiok connectors and two-way valves

d. Chart recorder (strip chart)

e. Syringe (1-10 μL) and (0.1-1 μL)

f. Source of zero (water, impurity free) air

Two calibration methods were performed for each component examined. These methods are explained in Appendix H. The first calibration scheme is the 5-point calibration. After all components are examined, a 10-Point calibration is performed. The following sequence of events was used to obtain data equivalent to that shown in Figures 27 and 28 for the KB component. Figure 29 diagrams the apparatus. For details concerning construction of the apparatus see Appendix G. For experimental data collected using this process, see section 4.7.

a. The two-way valve is turned to allow zero (water, impurity free) air to purge the MIRAN 80 cell.

b. After purging the cell for 5 min, the system is closed by the toggle and two-way valve switches. One must ensure that the MIRAN is at 1 atmosphere before isolating the system.

c. The GAIN is set until an absorbance background of +0.0005 is read for all wavelengths entered.

d. The circulating pump is started.

e. For a 5-point calibration, 1 μL is injected (in between readings) five times.

f. For a 10-point calibration, 0.1 μL is injected 10 times.

9 An actual sequence would be the following:

(1) The pump is started. Material (1 μL) is injected through the septum and 5 min are allowed to elapse.

(2) The circulating pump is turned off, the system is checked to ensure that the pressure is 1 atmosphere, then the analysis sequence started.

(3) After completion of one analysis routine, the clear button is depressed, and the analysis routine halted.

(4) The pump is turned on and the next injection made. (Do not purge between injections).

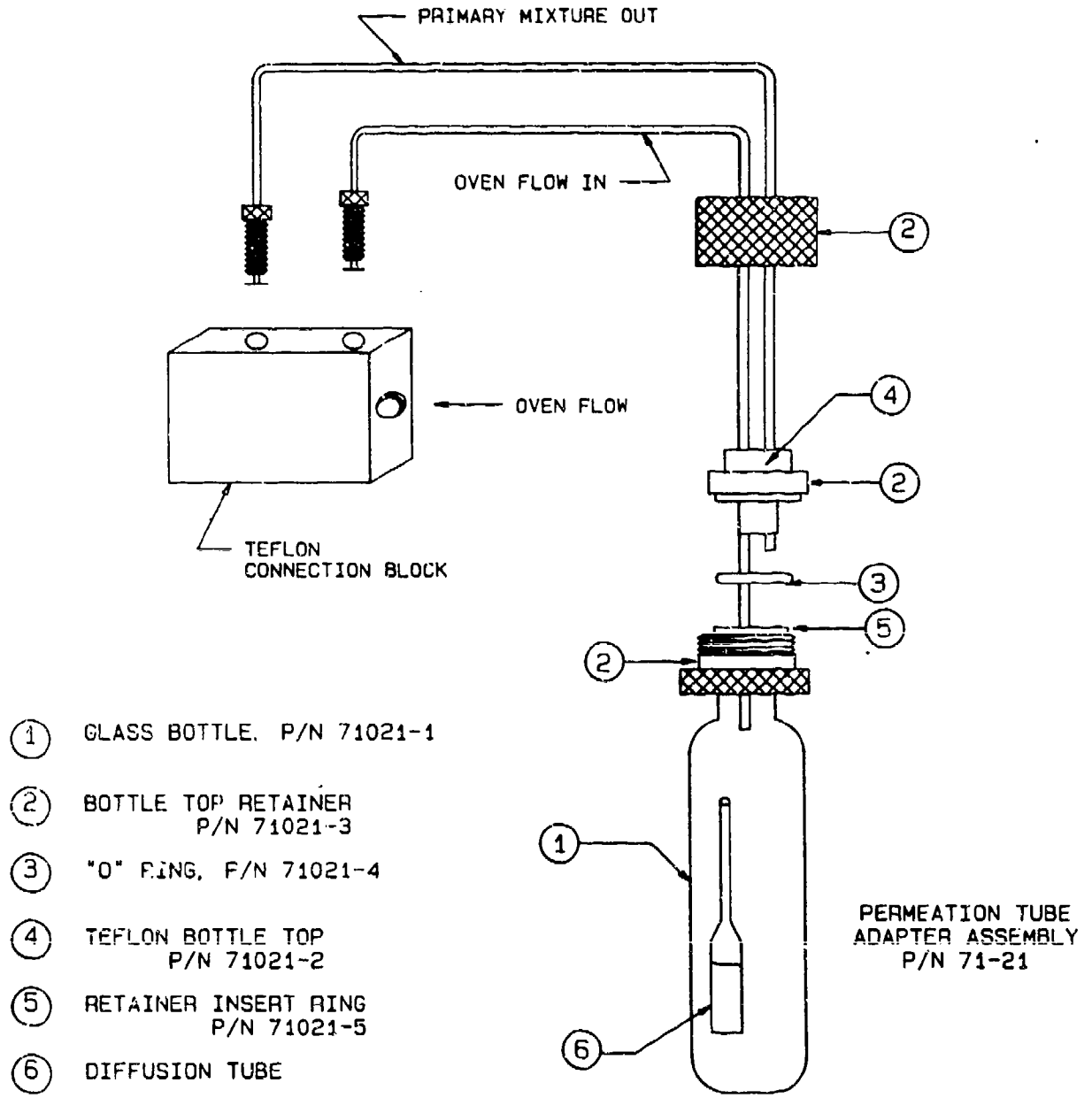


Figure 26. Gas Connections Permeation Tube Adapter

```
                    KB  (MIRAN 80)

The DETECTION LIMIT PROGRAM is based on an article by
HUBAUX AND VOS, ANAL CHEM 42,849(1970)

              **DETECTION LIMIT PROGRAM**

X IS THE CONC; Y IS THE SIGNAL.
THE TOTAL NUMBER OF INDEPENDENT CALIBRATION VALUES IS  10

                    X          Y

                 2.60     0.0013
                 5.21     0.0042
                 7.72     0.0064
                10.42     0.0098
                13.03     0.0128
                15.63     0.0162
                18.24     0.0196
                20.85     0.0223
                23.45     0.0245
                26.06     0.0276

The slope is       0.00111; The intercept is-     -0.0019 .
The correl. coeff.=0.99912.The std. error of est.=     0.00040
The two tail P level is 0.05. The CONFIDENCE  LEVEL is 95% (D.F.=  8).
The chosen Student's t value is   2.306

                          10 CALIBRATION STANDARDS
Yc, using eqn [16],is      -0.001 .
Assuming parallel confidence lines, the DETECTION
LIMIT, XD, is    1.96260 .
The XD based on eqn [15] and Y=Yc is      1.931 or      0.000
```

Figure 27. KB Detection Limit (10 Point)

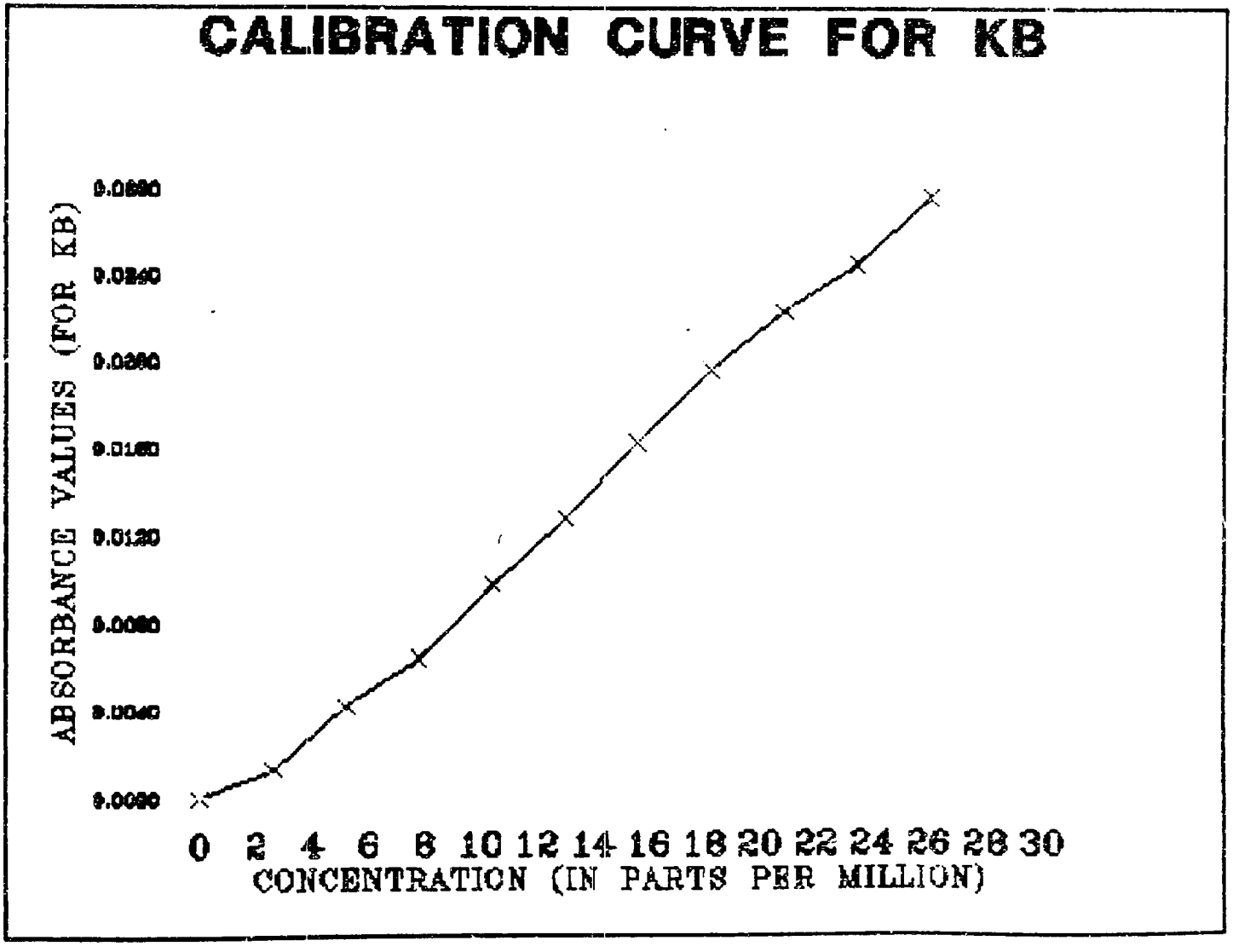


Figure 28. MIRAN KB 0014 Calibration Curve

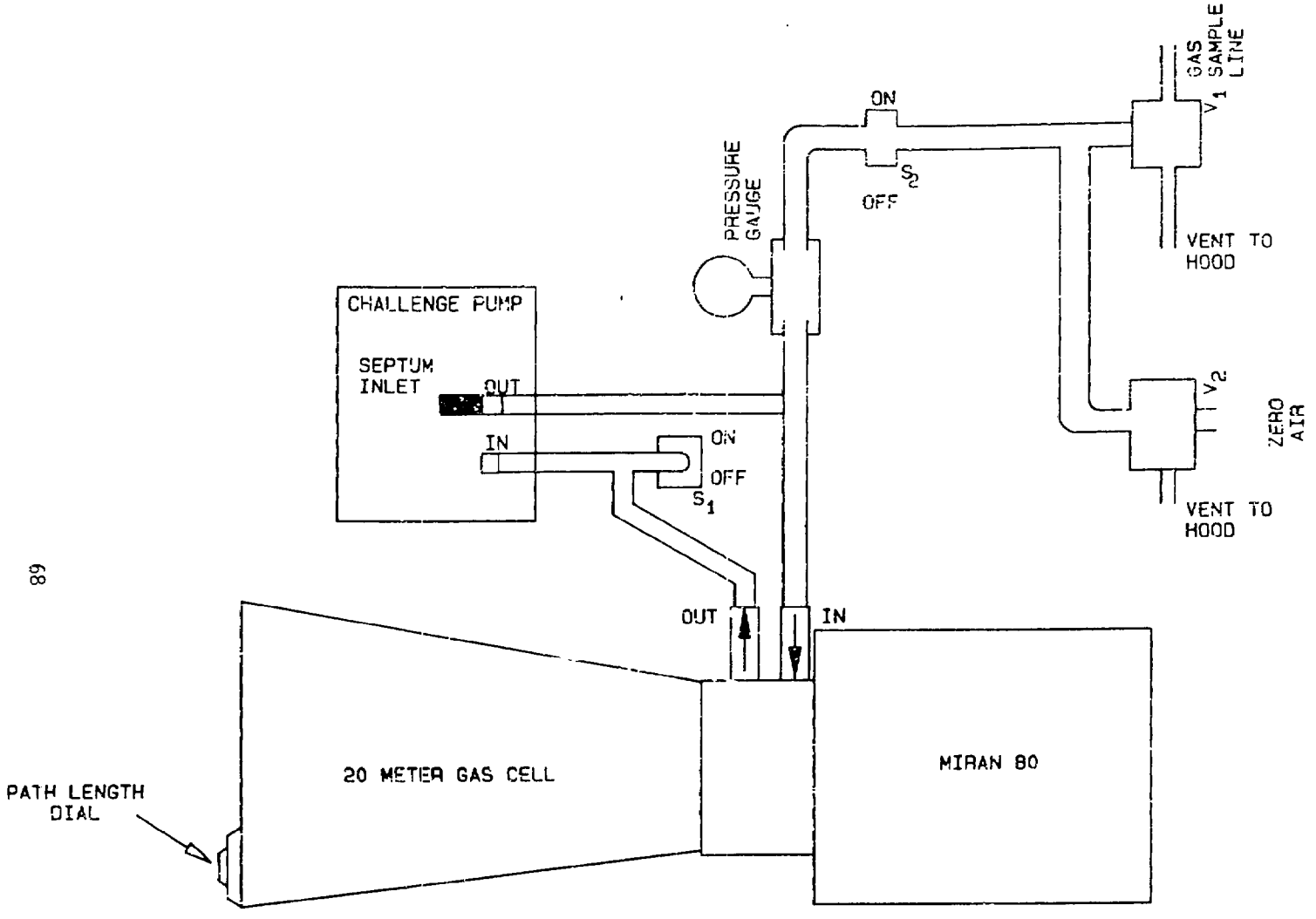


Figure 29. Closed Loop System (MIRAN 80)

(5) After completion of the desired number of injections, a scan of the final concentration in the cell is taken to obtain an infrared spectrum from 2.5 to 14.5 μm.

(6) The system is then opened and purged with zero air until the same or lower baseline absorbance readings are achieved. Baseline Absorbance Readings lower than ±0.0005 μm required gain resetting.

4.3.2 Continuous Gas Flow Method.

The second method of calibration, continuous gas flow, is performed in the same manner except the sample source is the SpanLab Gas Generator instead of liquid injections. For this method, the following sequence is initiated:

a. The MIRAN is purged with zero air, and a background reading is taken.

b. The two-way valves are turned to allow zero air from the SpanLab 580-3C to purge the MIRAN.

c. The GAIN is set until the values of absorption are within the +0.0005 range.

d. A background absorption value is taken to ensure stability of the MIRAN.

e. The toggle switch on the SpanLab is moved from standby to challenge. The component vapor then mixes with the zero air dilution flow gas.

f. A timer is set to ring every 3 min for the first 9-12 min, then every 10-15 min thereafter. An analysis is taken by depressing the analysis button on the MIRAN.

g. Readings are taken until the values for absorbance stabilize, thereby indicating concentration equilibrium.

This process was repeated for three concentrations of each component of interest. Runs were also repeated to check MIRAN reproducibility (section 4.7). NOTE: Once the SpanLab has been calibrated, no further calibration is required. The diffusion rate is constant; therefore, concentrations are dependent on dilution flow of the zero air feed into the diffusion holding chamber.

4.4 Concentration Determination.

We used three methods of determining concentrations. They are:

a. Bubbler sampling (YL and TEP samples)

b. Diffusion tube weight loss (KB, YL, TEP, and QL samples)

c. Sample injection computation (KB and YL samples)

4.4.1 Bubbler Sampling.

Bubbler sampling involved pulling each component through a solvent filled bubbler at the specific gas flow dilution level for a specified time period. This sample was then analyzed by GC against known concentration levels. The standards were well within bubbler sampler ranges. The following sequence demonstrates how we arrived at our concentration levels:

$$\text{Conc (wt/l)} = \text{wt/mL} \times \text{vol (mL)/sampling rate (min}^{-1}\text{)} \times \text{time (min)} \quad (4)$$

Where:

Cnc (wt/l) = concentration (weight/liter)

wt/mL = weight/milliliter

vol = volume of solvent in bubbler

sample rate (L/min) = (liters/minute)

time (min) = time sampled (minutes)

Note: No data were provided using this technique as a consequence of ineffective solvents and inadequate GC performance.

4.4.2 Diffusion Tube Weight Loss.

Diffusion tube weight loss required the measuring of the diffusion tube exactly at the end of several 24 hr periods to determine the rate at which the component diffused from the tube.

4.4.3 Sample Injection.

Sample injection requires knowing the amount of sample that is injected into the system. Concentration is then calculated using these equations provided by Foxboro.

Specific for gas samples:

$$C_{ppm} = \frac{v_{-i}}{v_s} \quad (5)$$

Where:

C_{ppm} = Concentration in parts-per-million

v_i = the microliters of gas injected

v_s = the 5.64 L of diluent volume in the closed loop system

Specific for liquid samples:

$$Cppm = \frac{DV_1}{M} \quad \frac{RT}{P} \quad \frac{* 10^3}{V_S} \qquad (6)$$

Where:

Cppm = Concentration in parts-per-million

Vi = Microliters of liquid sample injected

Vs = 5.64 L (cell volume)

D = Density of liquid in g mL^{-1}

R = 0.08206 atm^{-1} degree K mole

T = Temperature in degrees Kelvin

P = Pressure in atmospheres

M = Molecular weight of sample

4.4.4 Gas Generated Sample Method.

Concentration using the gas generated sample method is calculated using the following equation:

Concentration of Bubbler = wt mL^{-1} x volume of bubbler (mL) (7)

Bubbler sampling rate mL min^{-1} x time sampled (min)

4.5 Tabulated and Graphical Data.

The tabulated and graphical data obtained throughout this section were computer-generated unless otherwise indicated. The programs used to generate curves and determine slopes, intercepts, standard deviations, and confidence lines were written[2,3] from the theory provided by Hubaux and Vos.[4]

4.5.1 Detection Limit Results.

The first minimum detectable limit value obtained for KB is 1.931 ppm. The data used to calculate this value was produced by making

---

[2]Program, Management Systems Division, Information Systems Command, Aberdeen Proving Ground, MD, 1970.

[3]P-Matrix Program, Version 2.5, Foxboro, Incorporated, Foxboro, MA, June 1976.

[4]Hubaux, Andre, and Vos, Gilbert, "Decision and Detection Limits for Linear Calibration Curves," Anal. Chem. Vol 42, p 849 (1970).

10 consecutive 0.1-µL injections into the closed loop system and obtaining an absorption value for each 0.1 µL. The cell was not purged between injections,and the circulation time was 5 min per injection. The data used to compute this value is also plotted and labeled (Figures 27 and 28) MIRAN 80 using the Hubaux and Vos computer-based statistical program. This is the same data used for instrument calibration in section 4.3.

4.5.2 Lower Limits.

Because the desired range was parts per million, a 1-µL syringe was used to inject 0.01 µL of KB and YL. By doing so, the limits of the instruments were approached. For the components KB and YL, 0.01 µL equates to 0.26 and 0.2125 ppm, respectively. It was not advisable to use either unit at this level because the manufacturer recommended unit operation at twice the noise level. The noise level for the MIRAN 80 and 980 were 0.0002 and 0.0005 absorbance units, respectively. These values are based on a performance check of both units. From the data generated, the MIRAN was operating very close to its noise level at 0.01 µL (i.e., 0.0004 and 0.0007 absorbance units, respectively). Consequently, all subsequent injections to calibrate either MIRAN unit were made in 0.02 µL amounts or greater. This resulted in absorbance readings of 0.0007 and 0.001 on the MIRAN 80/980, respectively for both components analyzed.

4.5.3 Reported Minimum Detectable Limit.

The mimimum detectable limits for KB and YL were cited as 0.52 and 0.425 ppm, respectively. These values were obtained from the weight loss of the diffusion tube for KB and YL and the correlation of the MIRAN 80's absorbance versus concentration for six trials. Graphs of data (Figures 30-35) present the curve for a typical calibration using the MIRAN 80. Shown are graphs of the connected points followed by the least square fit of that same data. This data was extracted from trial 1 (Tables 25 and 26) of section 4.7.

4.6 Spectral References.

As a consequence of the similarity of functional groups among the hydrolysis and degradation products of QL, the following reference IR data were gathered. This information is critical to the selection of appropriate wavelengths for the MIRAN. Various parameters and instrumentation operating conditions can be obtained by contacting the individual organization on the Aberdeen Proving Ground (Edgewood Area). Without this information, there is no absolute method to determine whether or not the wavelength chosen for a particular component is not also found in the IR spectrum of another QL component.

4.6.1 IR Data.

Determination of the specific wavelength ranges for analysis by the single beam instruments (MIRAN 80 and 980) were made from the following spectrographic data. These data were obtained from two sources.

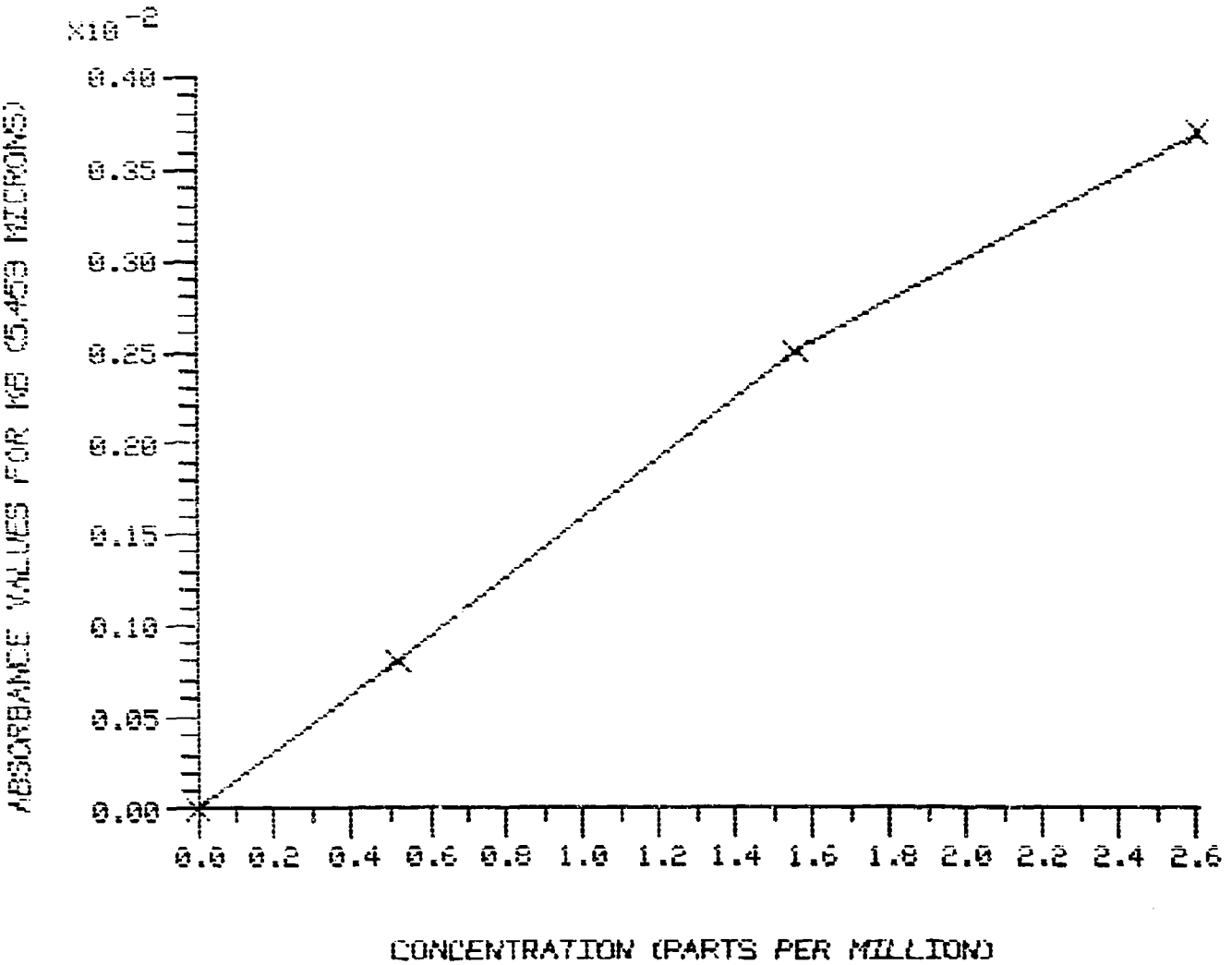


Figure 30. 3-Point Calibration Curve for KB

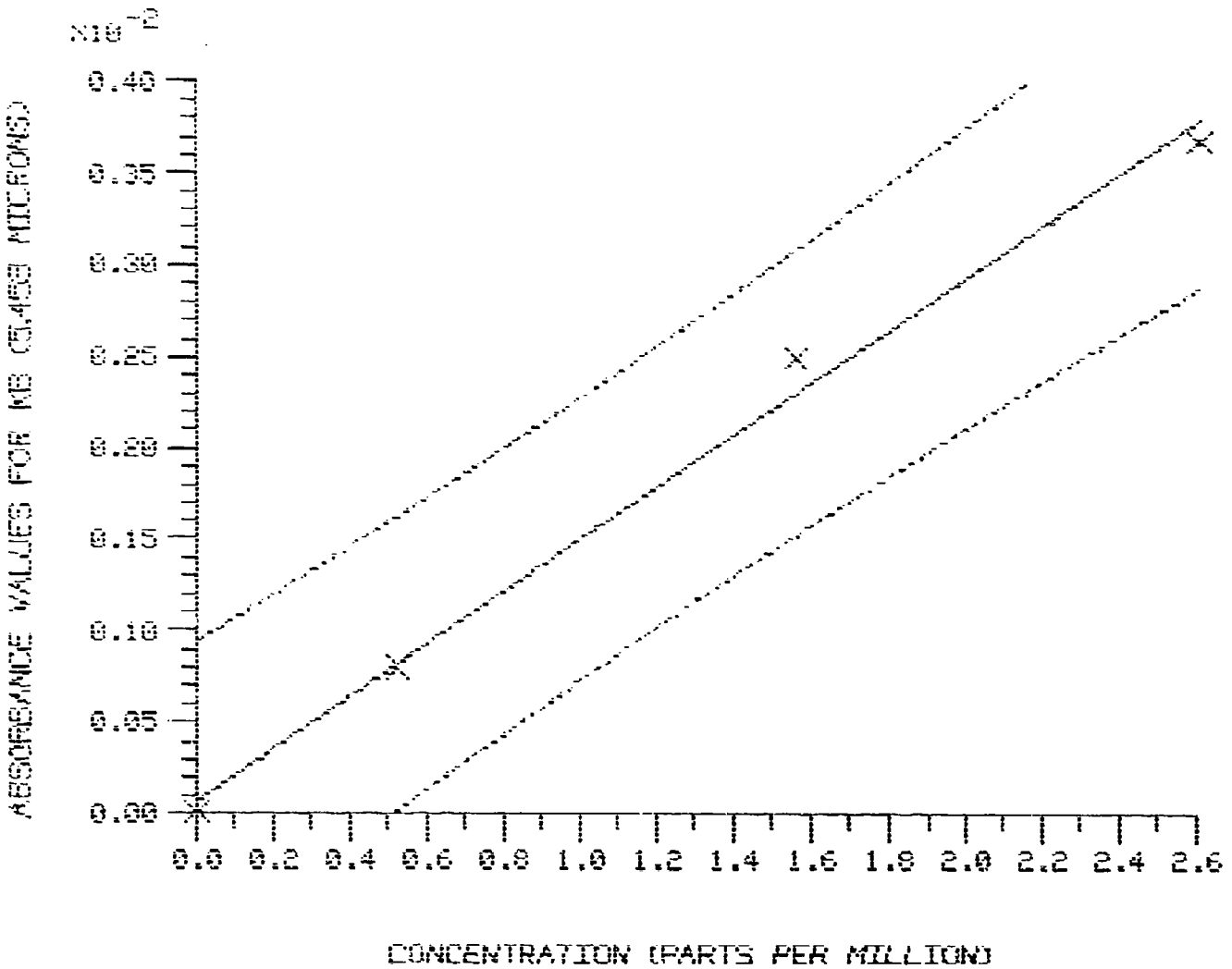


Figure 31. KB Calibration Curve with 95% Confidence Lines

```
DATA SET NO.  1                    MIRAN.KBLGJ

X MEAN =       1.17000             X STD.DEV.=       1.15303
Y MEAN =     1.750000-03           Y STD.DEV.=     1.666333-03

 Y= 6.4407-05+1.4407-03X**1
 ANAL.OF VAR.          DF    SUM OF SQUARES     MEAN SQUARE       STD. ERROR
 DUE TO REG.            1       8.278136-06       8.278136-06       2.877175-0
...3
 ERROR ABOUT REG.       2       5.186440-08       2.593220-08       1.610348-0
...4
 TOTAL                  3       8.330000-06
  F TEST:       319.222
  COEF.OF DETERMINATION:    .993774
```

Figure 32. Statistical Values for Figure 31

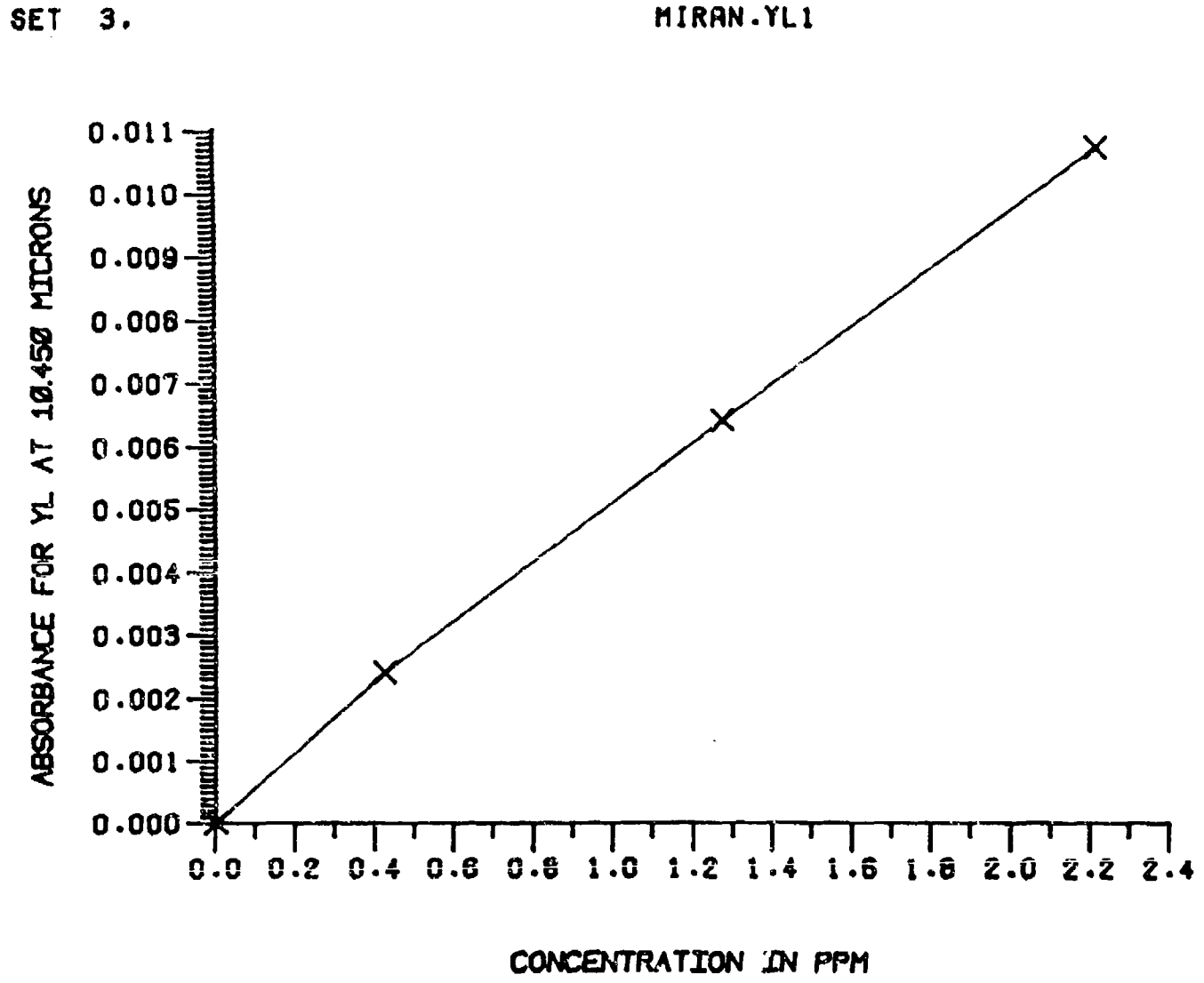


Figure 33. YL Calibration Curve (3 Points)

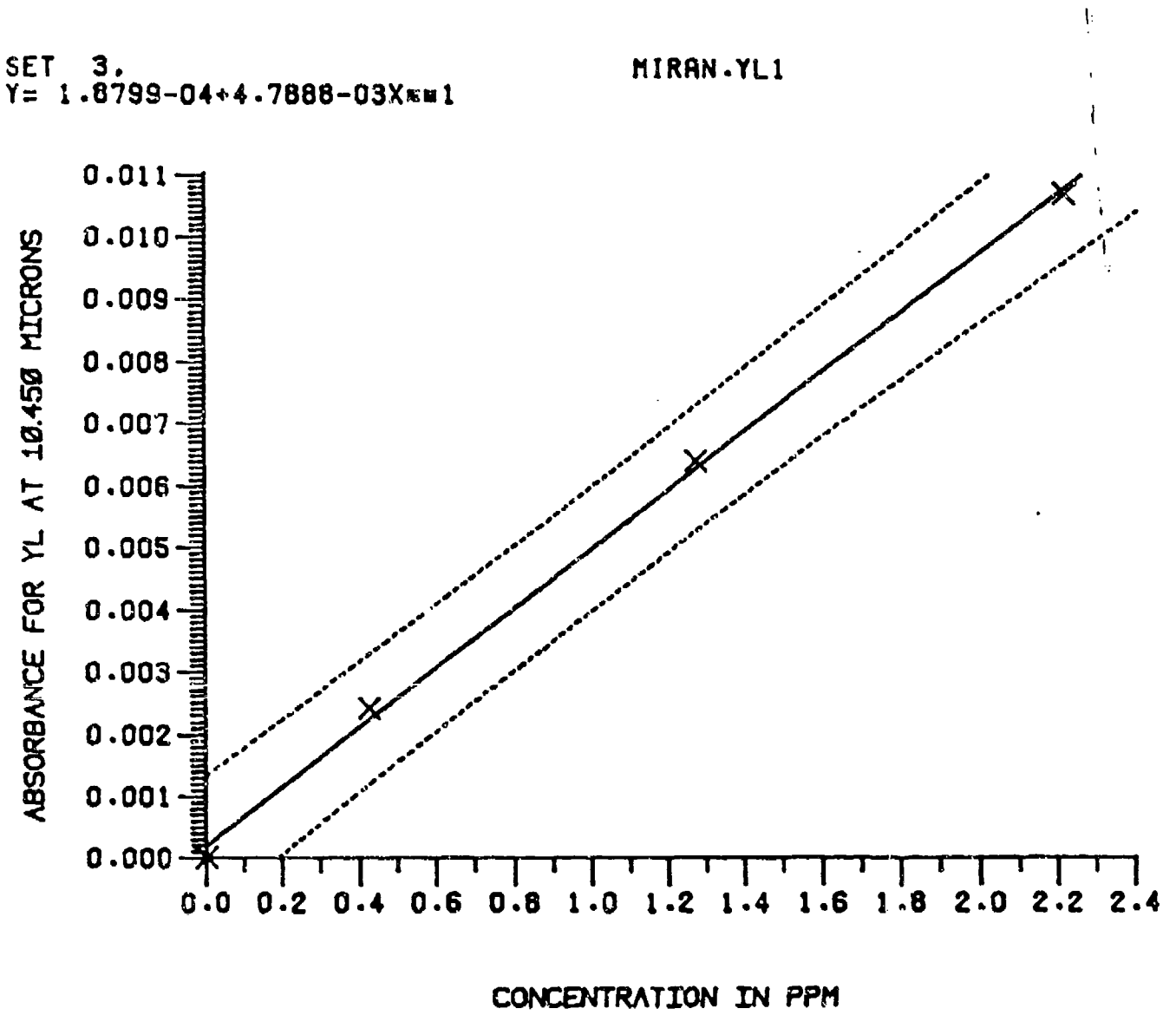


Figure 34. YL Calibration Curve with 95% Confidence Lines

DATA SET NO. 1 MIRAN.YL1

X MEAN = .978750 X STD.DEV.= .979910

Y MEAN = 4.875000-03 Y STD.DEV.= 4.695654-03

Y= 1.8799-04+4.7888-03X**1

ANAL.OF VAR.	DF	SUM OF SQUARES	MEAN SQUARE	STD. ERROR
DUE TO REG.	1	6.606055-05	6.606055-05	8.127764-0
...3				
ERROR ABOUT REG.	2	8.694504-08	4.347252-08	2.085007-0
...4				
TOTAL	3	6.614750-05		

F TEST: 1519.50

COEF.OF DETERMINATION: .999686

Figure 35. Statistical Values for Figure 34

The double beam liquid phase Fourier transform data were obtained from the Spectroscopy Branch, Analytical Division, Research Directorate, CRDEC. Gas Phase Fourier transform data were obtained from the Organic Environmental Chemistry Division of the U.S. Army Environmental Hygiene Agency. This section explains the liquid and gas phase data for QL and its breakdown products.

4.6.2 Liquid Phase Data.

Liquid phase data were generated by a Nicolet 10-MX Fourier Transform Infrared (FTIR) double beam system (Figures 36-46). For a complete explanation of how these data were used to select monitoring wavelengths for KB, YL, and QL, see Appendix F.

Wavelengths chosen for specific QL hydrolysis products were taken directly from the spectra. Selected values were then entered into the MIRAN over a banded range for digital scan analysis. The band was separated into 50 segments and the strongest 2-4 bands (absorption values) were selected for each of the components and entered into the MIRAN 80 before calibration. This process is described in Appendix H.

The Nicolet unit also provided a vapor phase spectrum for QL taken at a pathlength of 15.75 m and a pressure of 0.024 torr. The vapor phase spectrum compares favorably with the vapor phase spectrum obtained from the GC Fourier transform system (see Figures 39 and 57).

4.6.3 Vapor Phase Data.

Vapor phase data were generated by a DigiLab Gas Chromatograph FTIR Transform Infrared system. The spectra are from a single injection of QL which was hydrolyzed over 4-weeks. A 0.5-µL quantity of QL was injected onto a DB-5 megabore column for separation into its components, indicated by peak number. Raw data were used for MIRAN calibration. Absorption maximum were determined by digital scan techniques. Care was taken to avoid interference carbon dioxide and water. The final wavelengths used to determine minimum detectable limits were above 8.0 µm. The identity of each spectrum (Figures 47-72) can be obtained by looking at the peak table. All FTIR spectra are presented in units of wavenumber (x-axis) versus intensity (y-axis)

NOTE: It was necessary to obtain vapor phase IR spectra of QL components because our task is to monitor airborne particles at the parts-per-million level and lower. Although it is true that most IR spectra have fairly similar vapor phase spectra, we were not willing to risk monitoring at a wavelength that may not be present when a compound is in the vapor phase.

4.6.4 Method for Reading Peak Tables.

The GC-FTIR provides an absorbance versus time profile of the components as they are separated by the columnn and enter the IR unit. This absorbance versus time profile is termed Gram-Schmidt. Locate the Gram-Schmidt spectra for both pure KB and QL components (Figures 69 and 47). At the bottom of each spectra, locate the scale labeled scan

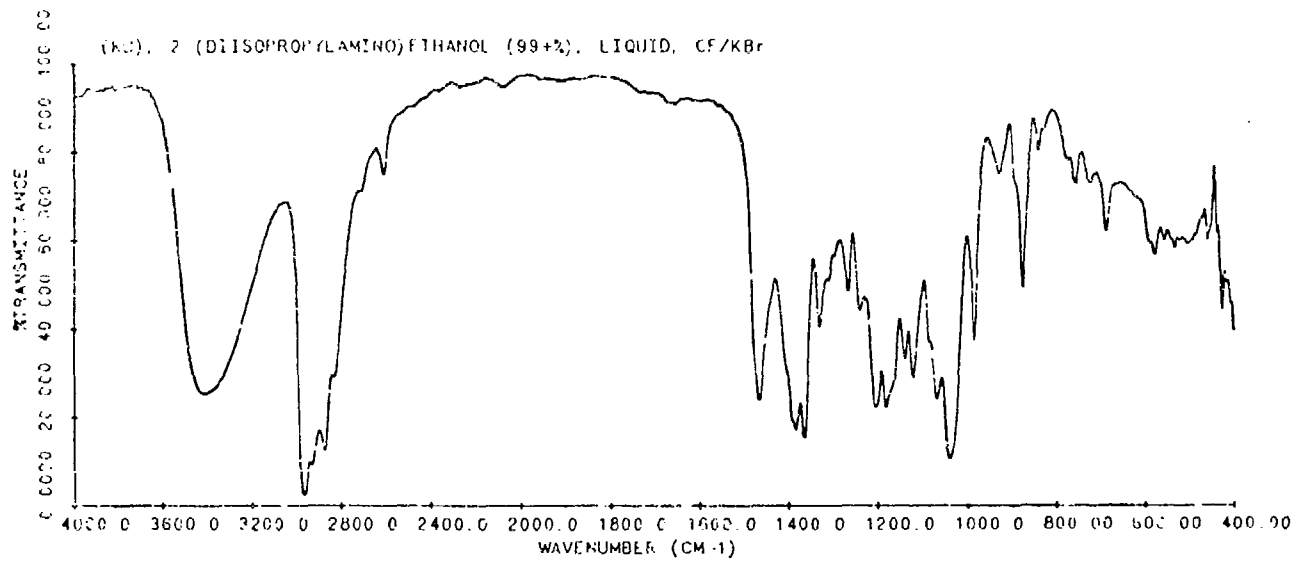


Figure 36. Liquid Phase FTIR Spectrum of KB

Text continues on page 113.

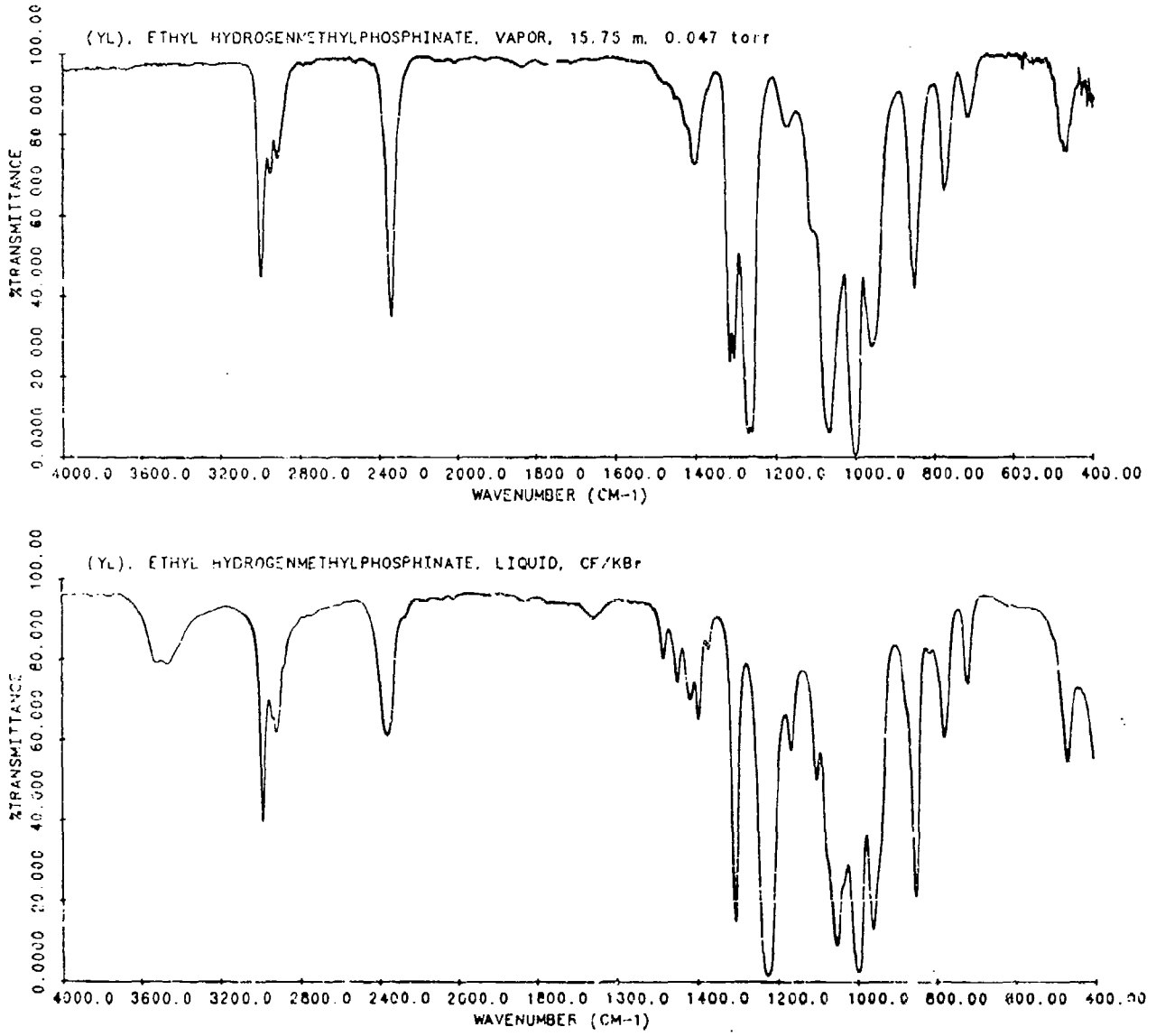


Figure 37. Liquid/Vapor Phase FTIR Spectrum of YL

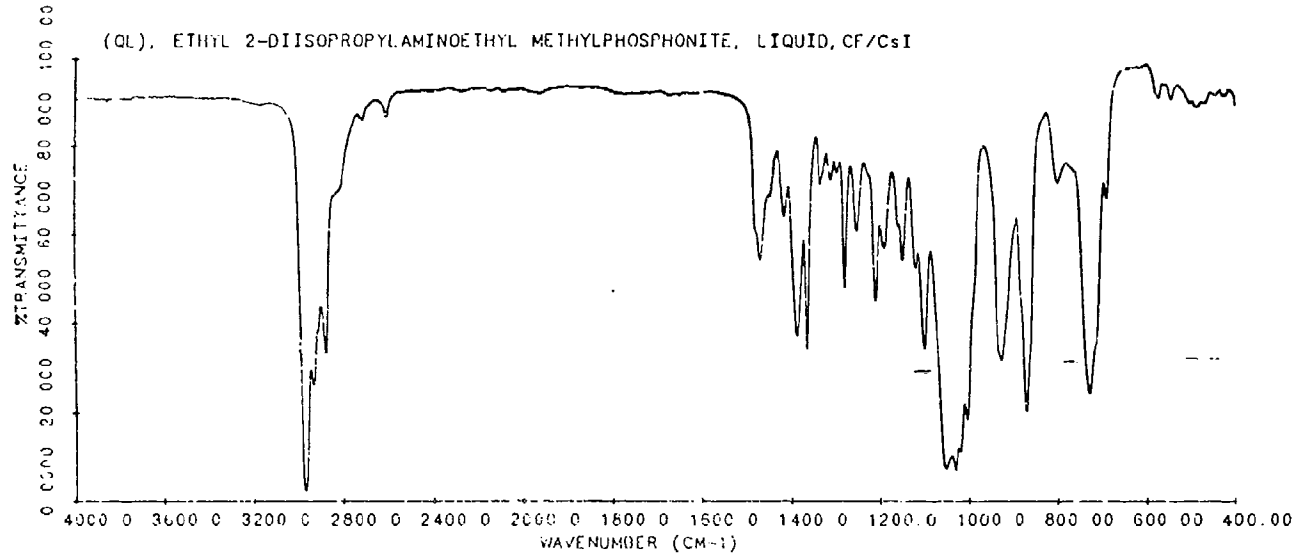


Figure 38. Liquid Phase FTIR Spectrum of QL

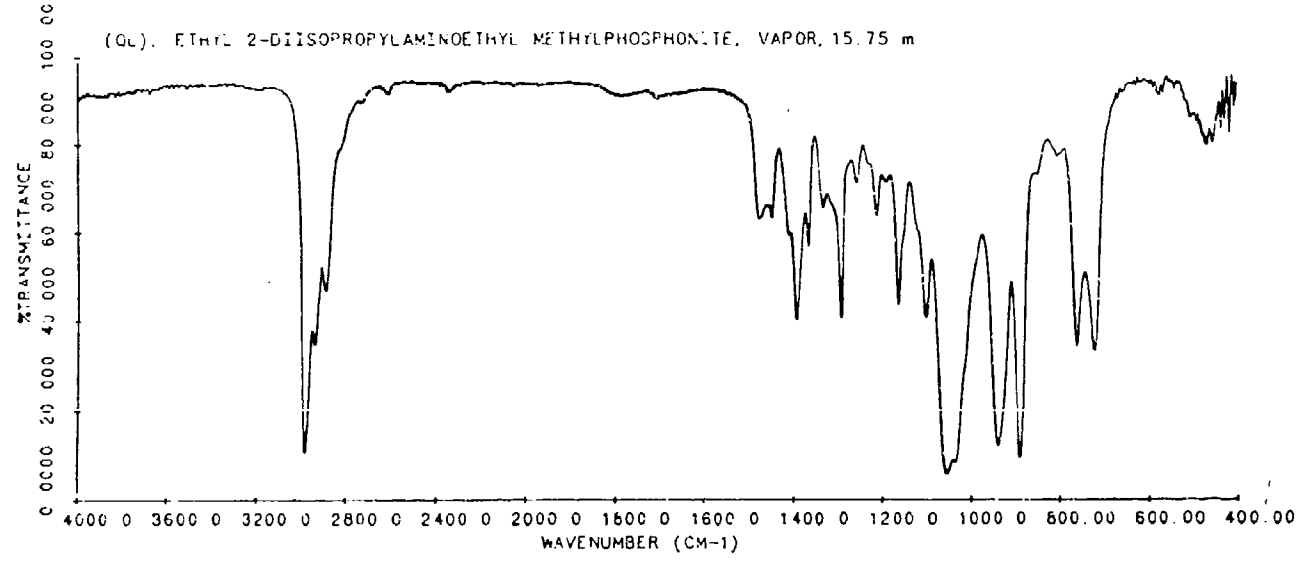


Figure 39. Vapor Phase FTIR Spectrum of QL

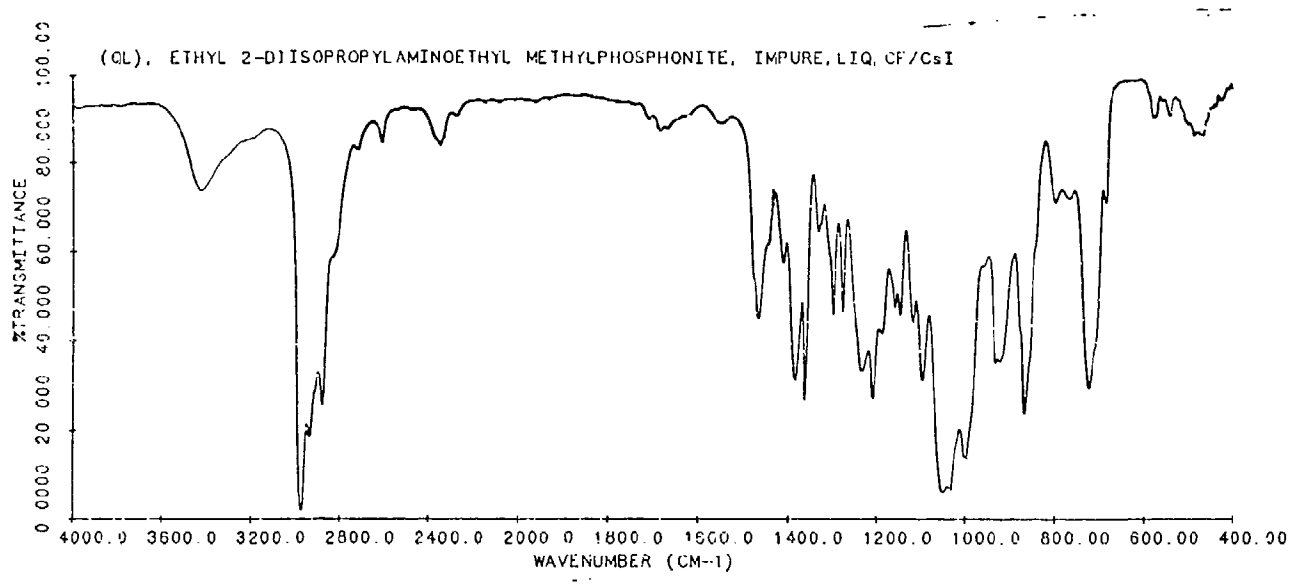


Figure 40. Liquid Phase FTIR Spectrum of Impure QL

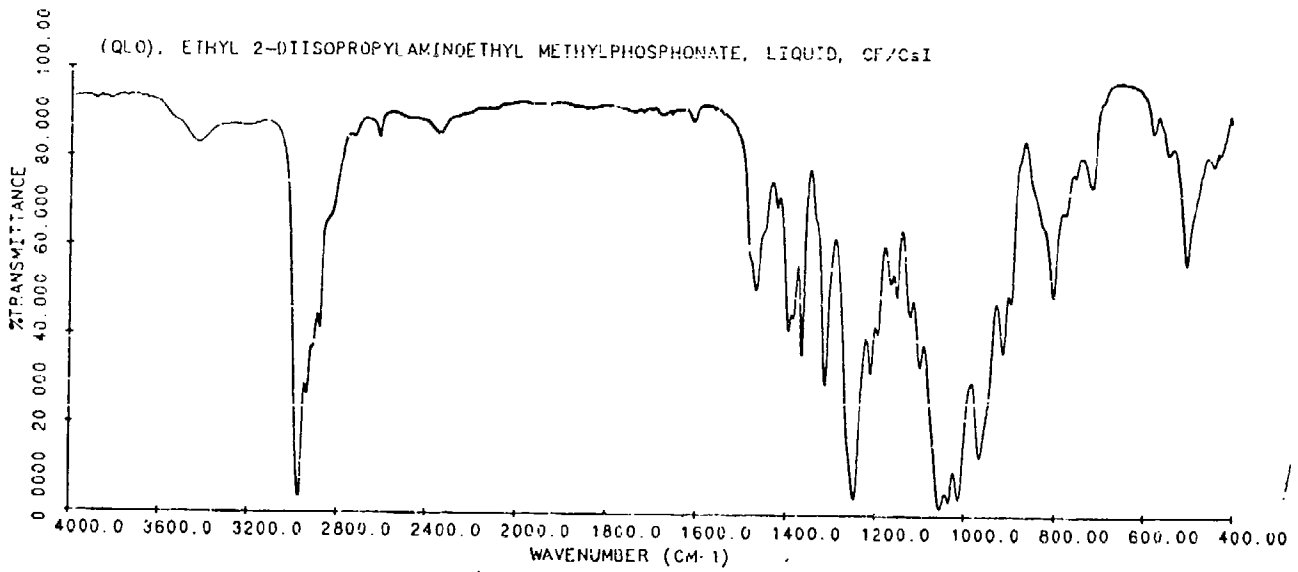


Figure 41. Liquid Phase FTIR Spectrum of QLO

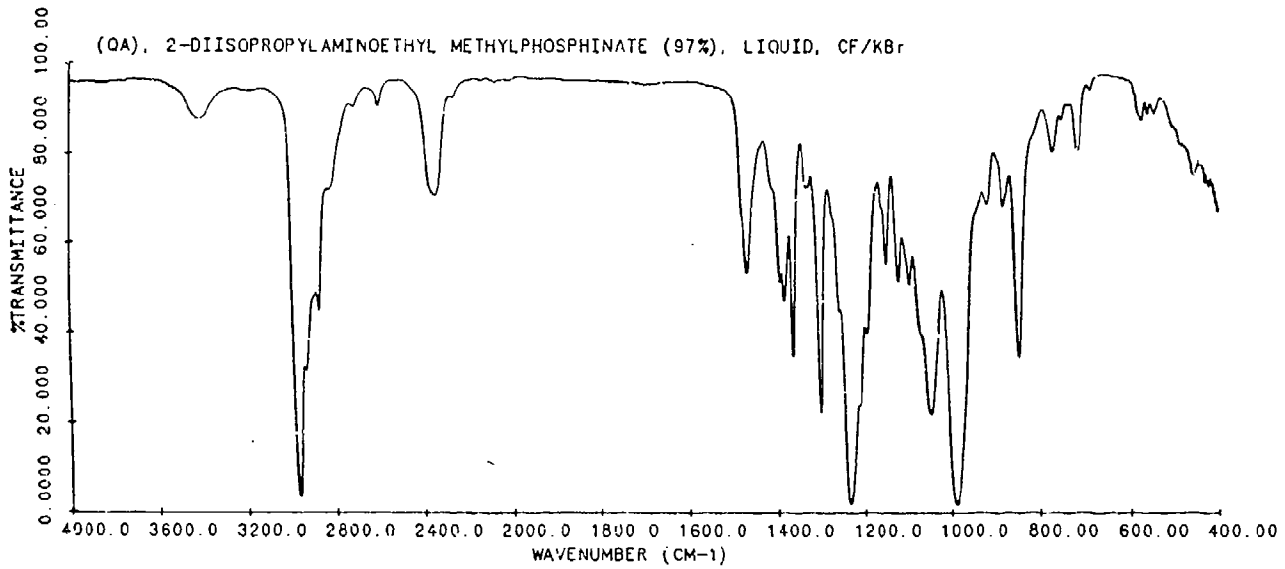


Figure 42. Liquid Phase FTIR Spectrum of QA

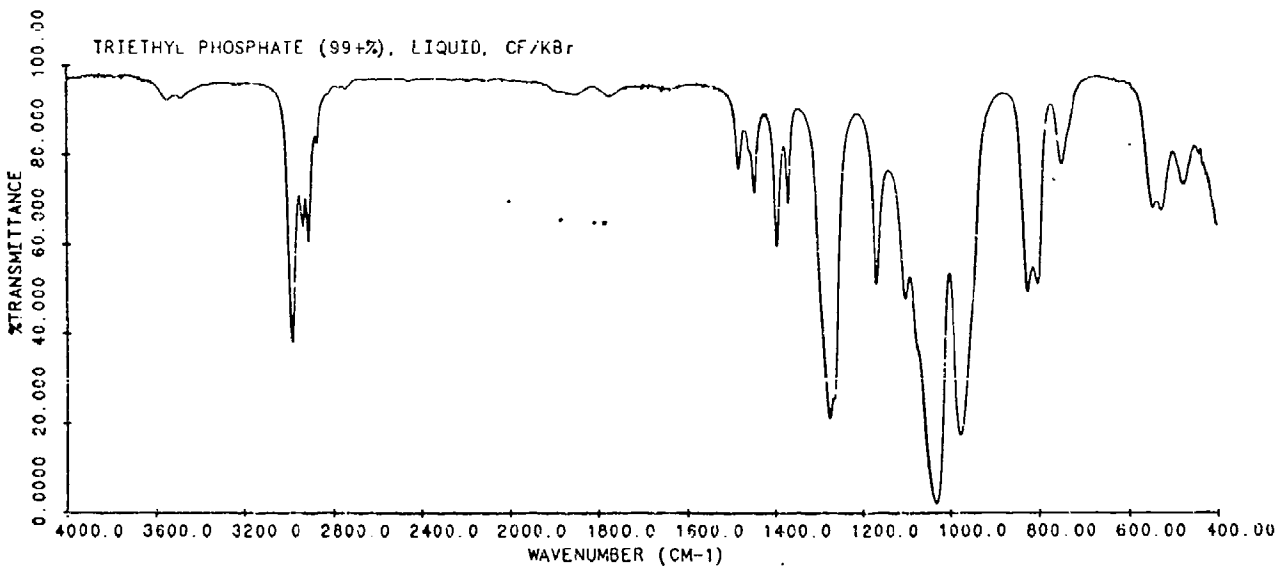


Figure 43. Liquid Phase FTIR Spectrum of TEPO

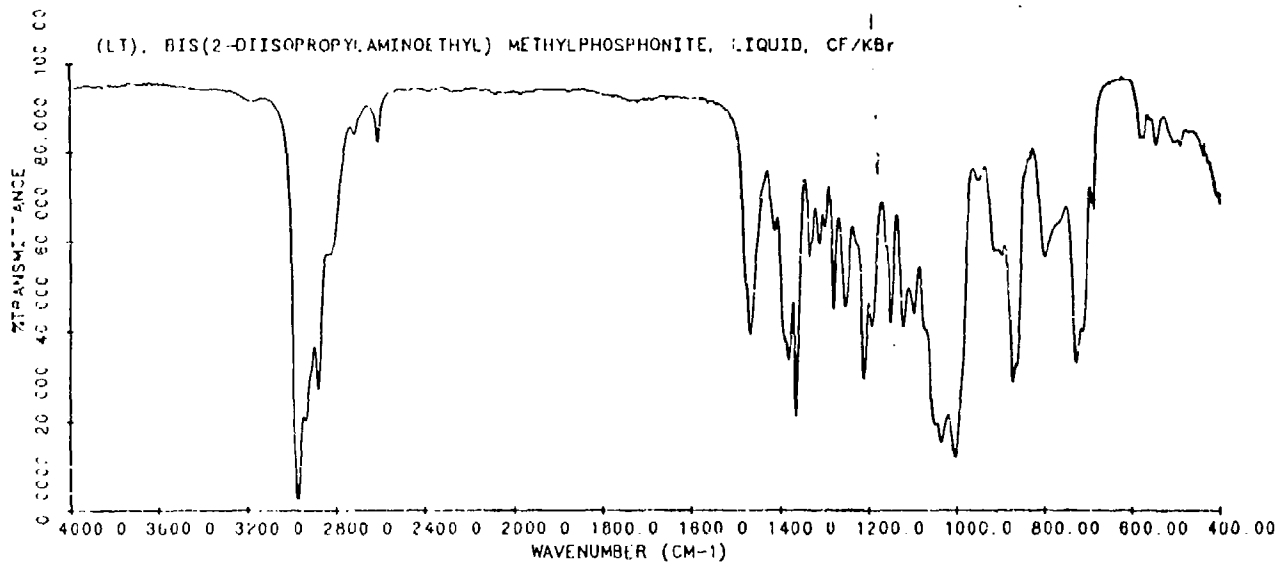


Figure 44. Liquid Phase FTIR Spectrum of LT

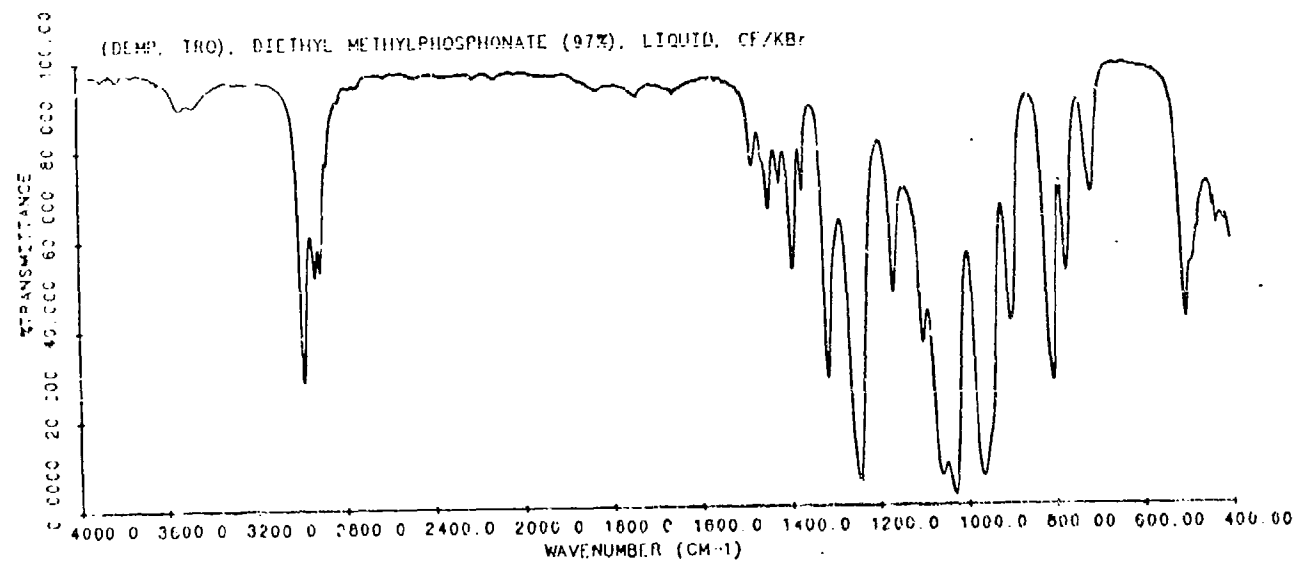


Figure 45. Liquid Phase FTIR Spectrum of DEMP

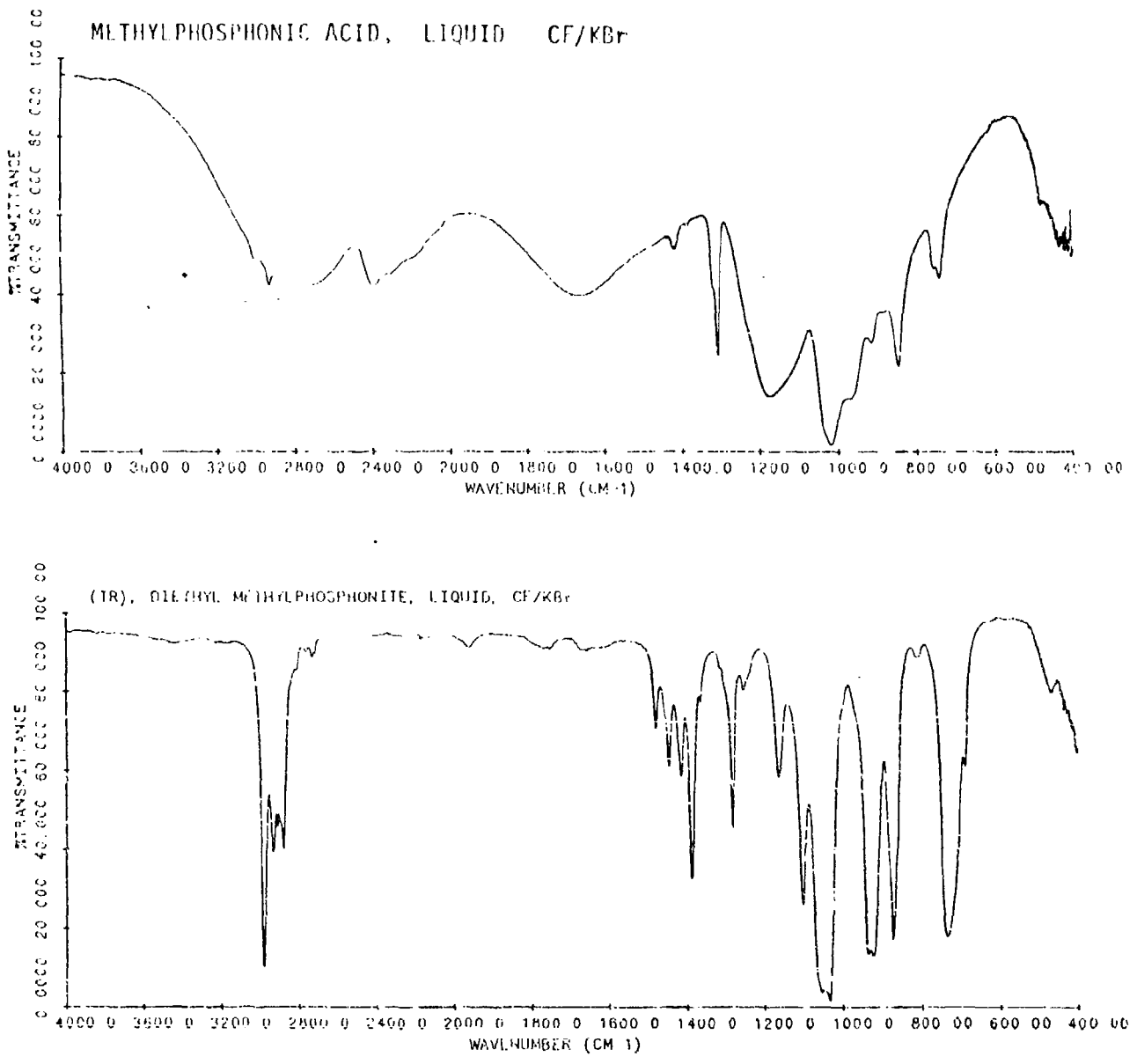


Figure 46. Liquid Phase FTIR Spectrum of Methylphosphonic Acid/TR

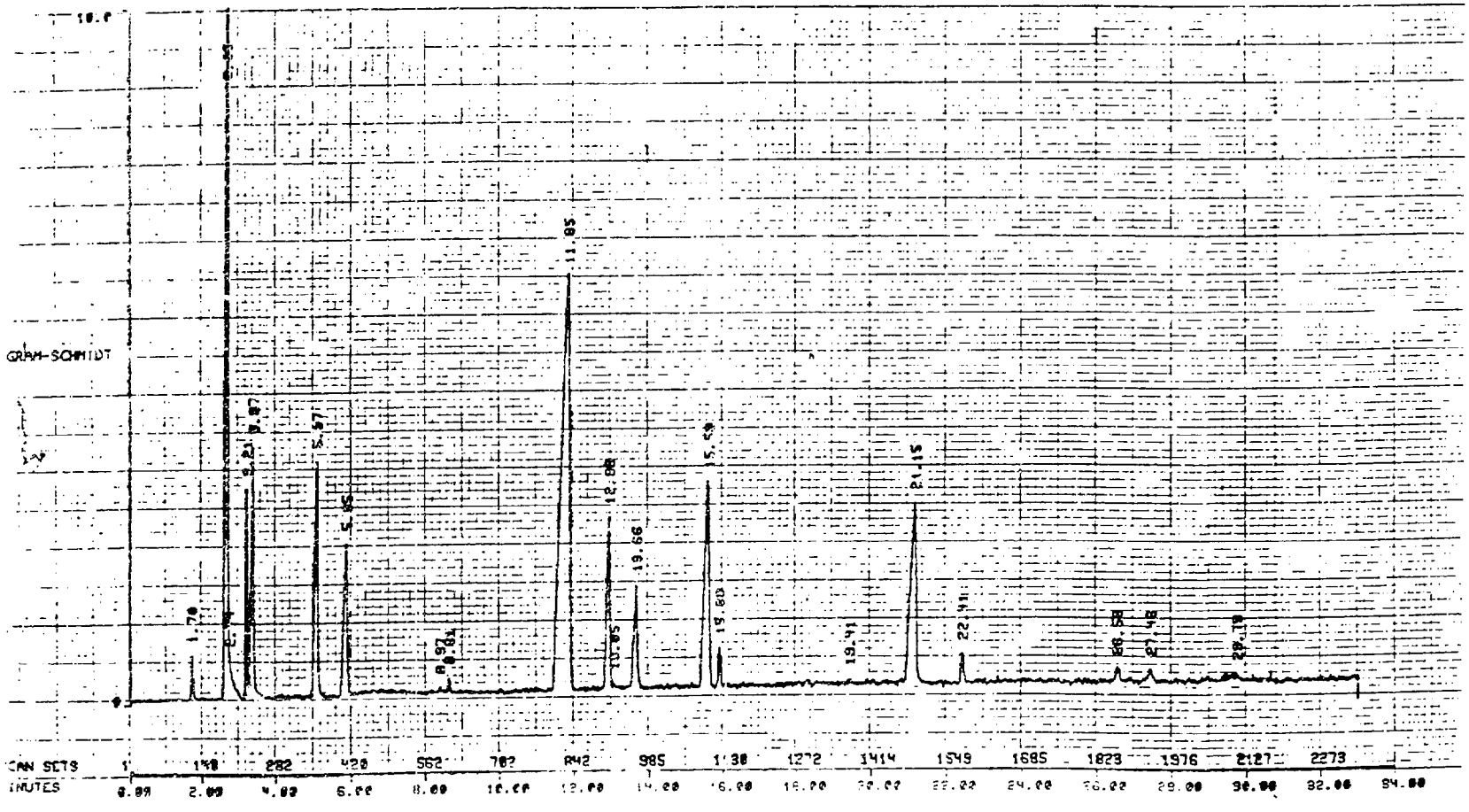


Figure 47. Gram-Schmidt for QL

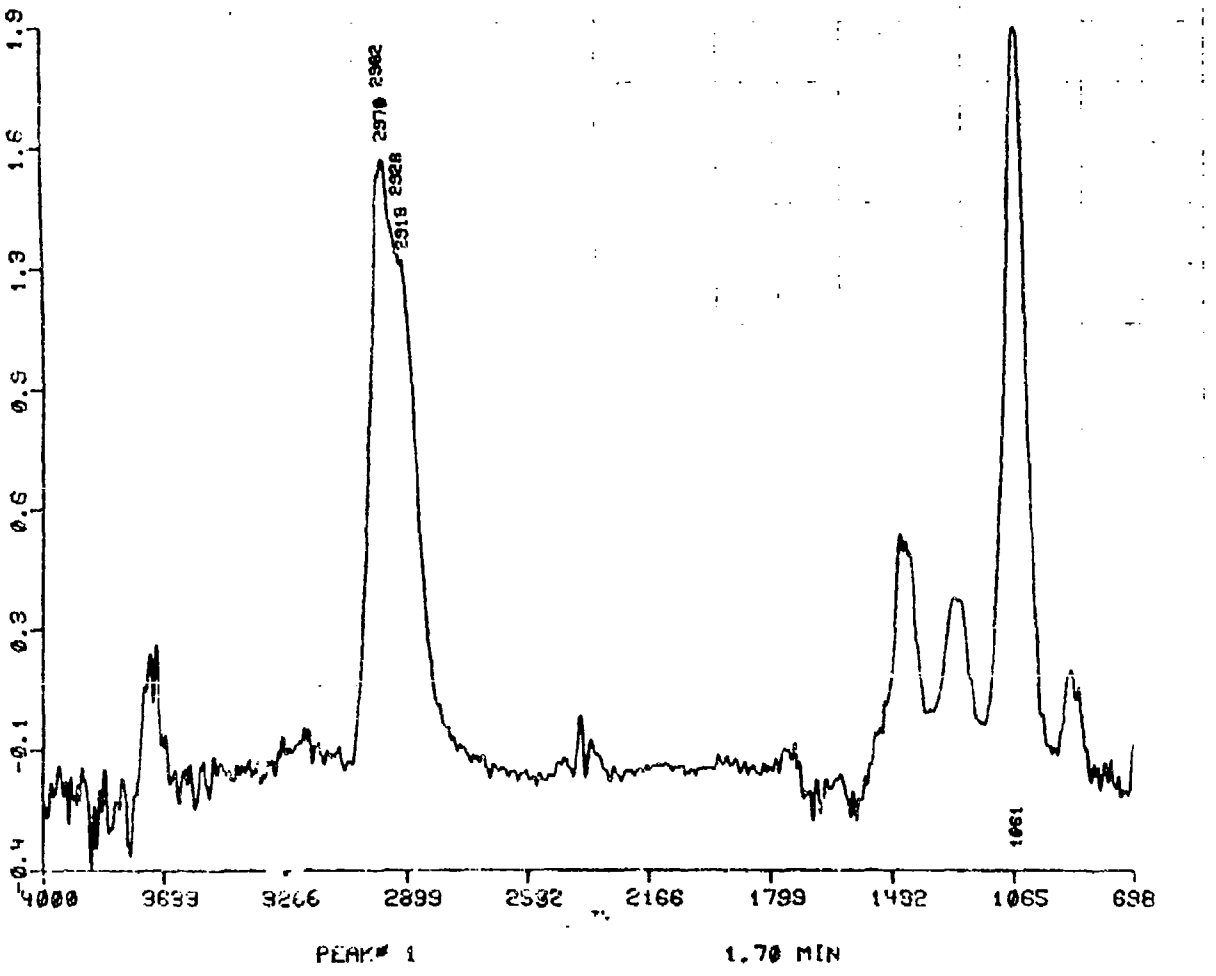


Figure 48. Peak No. 1 EtOH (Ethanol)

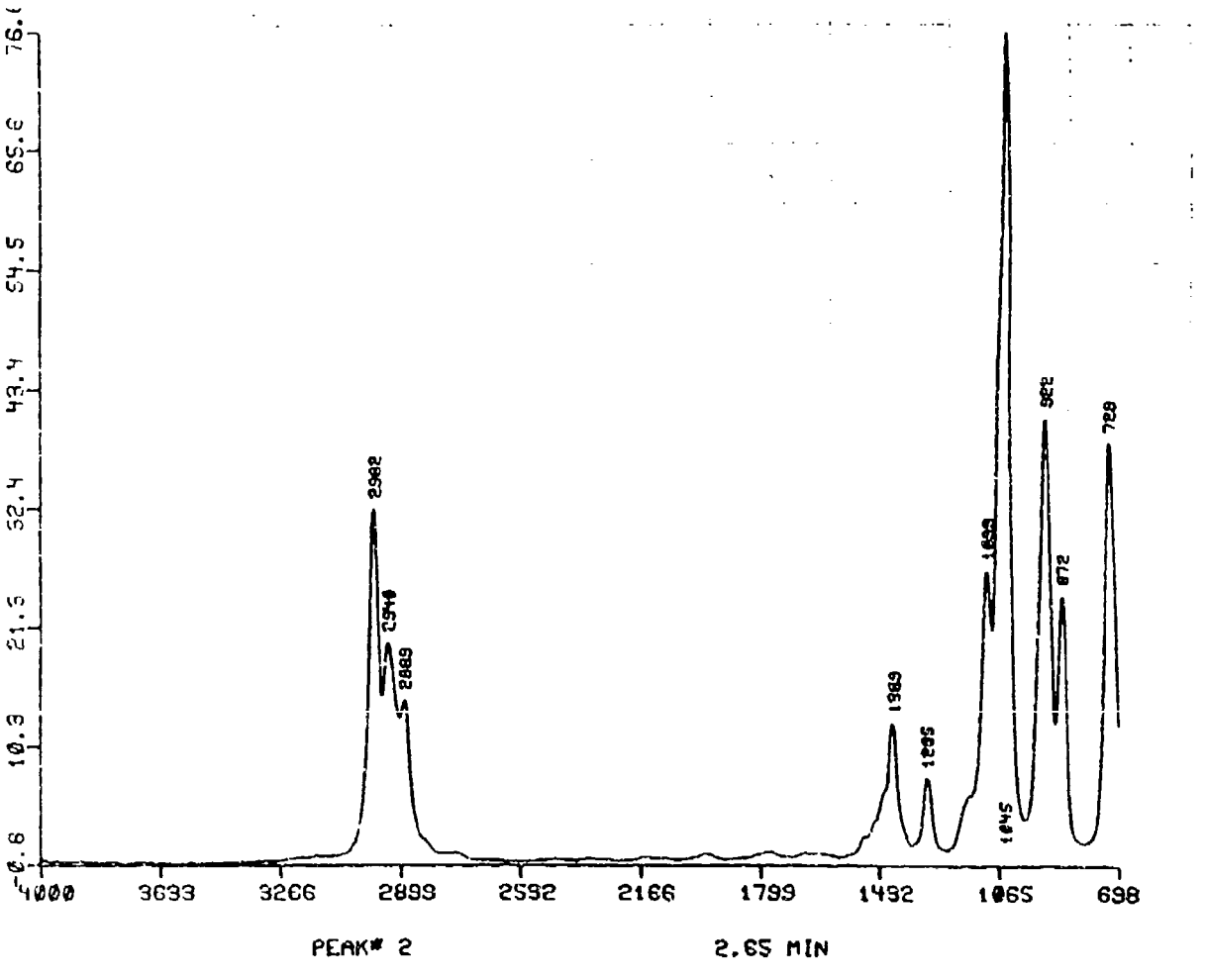


Figure 49. Peak No. 2 TR

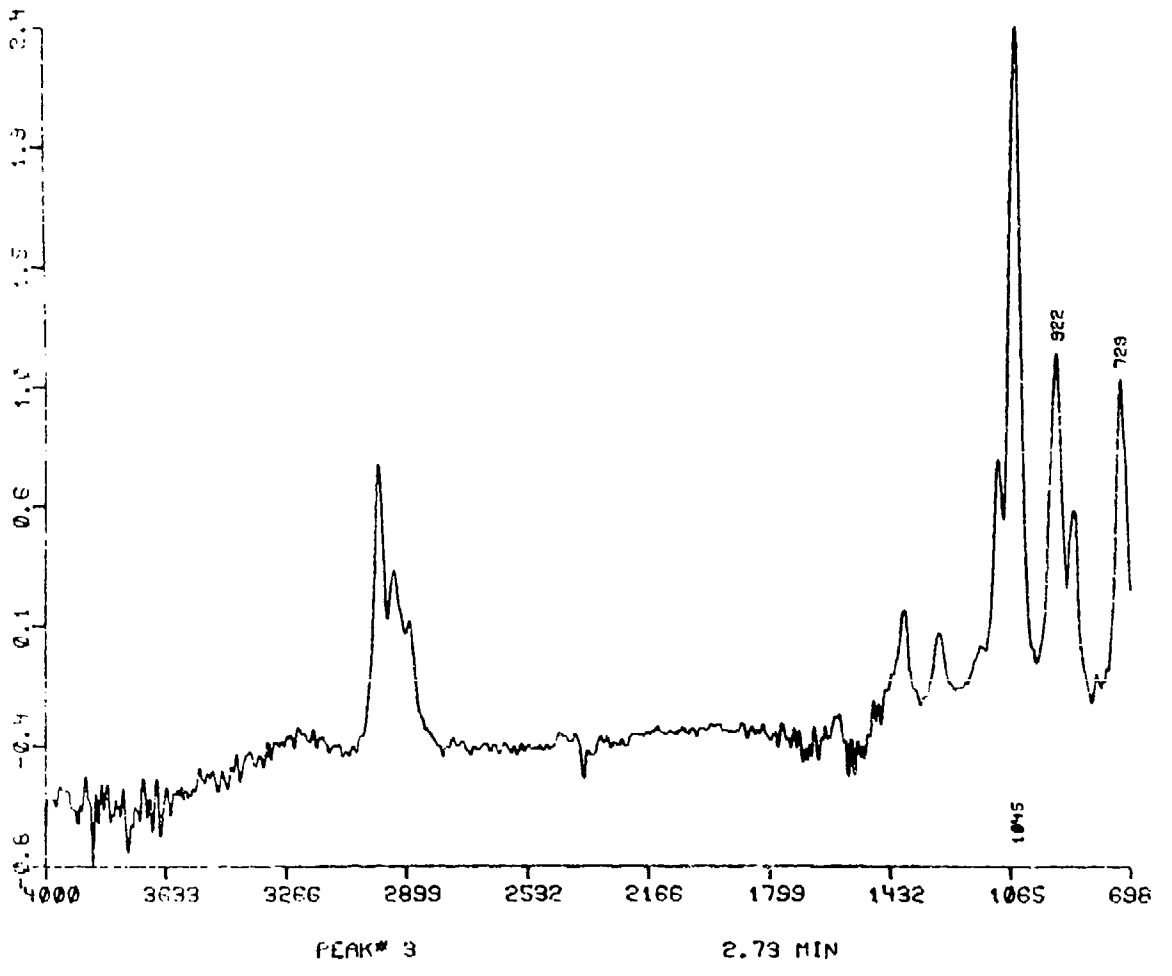


Figure 50. Peak No. 3 Unknown

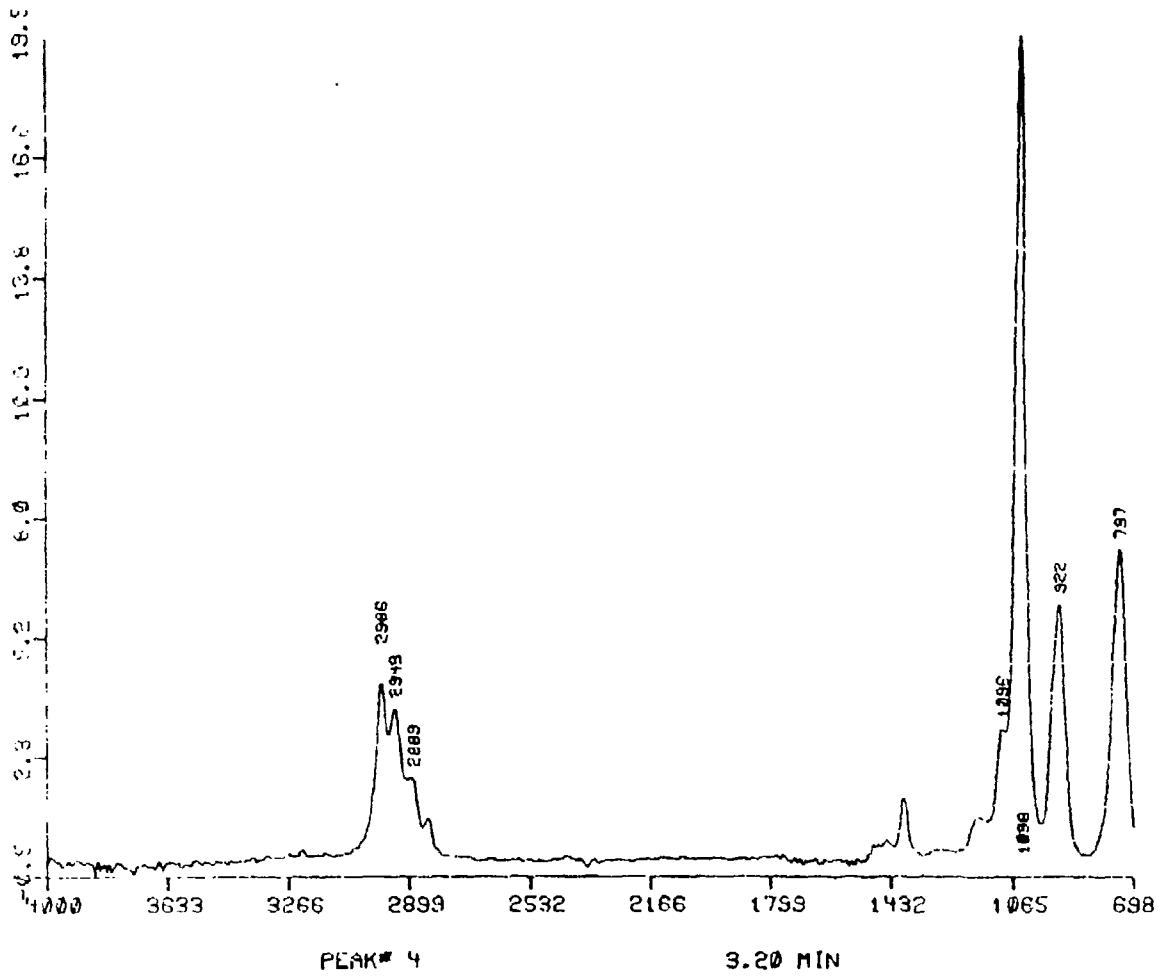


Figure 51. Peak No. 4 Unknown

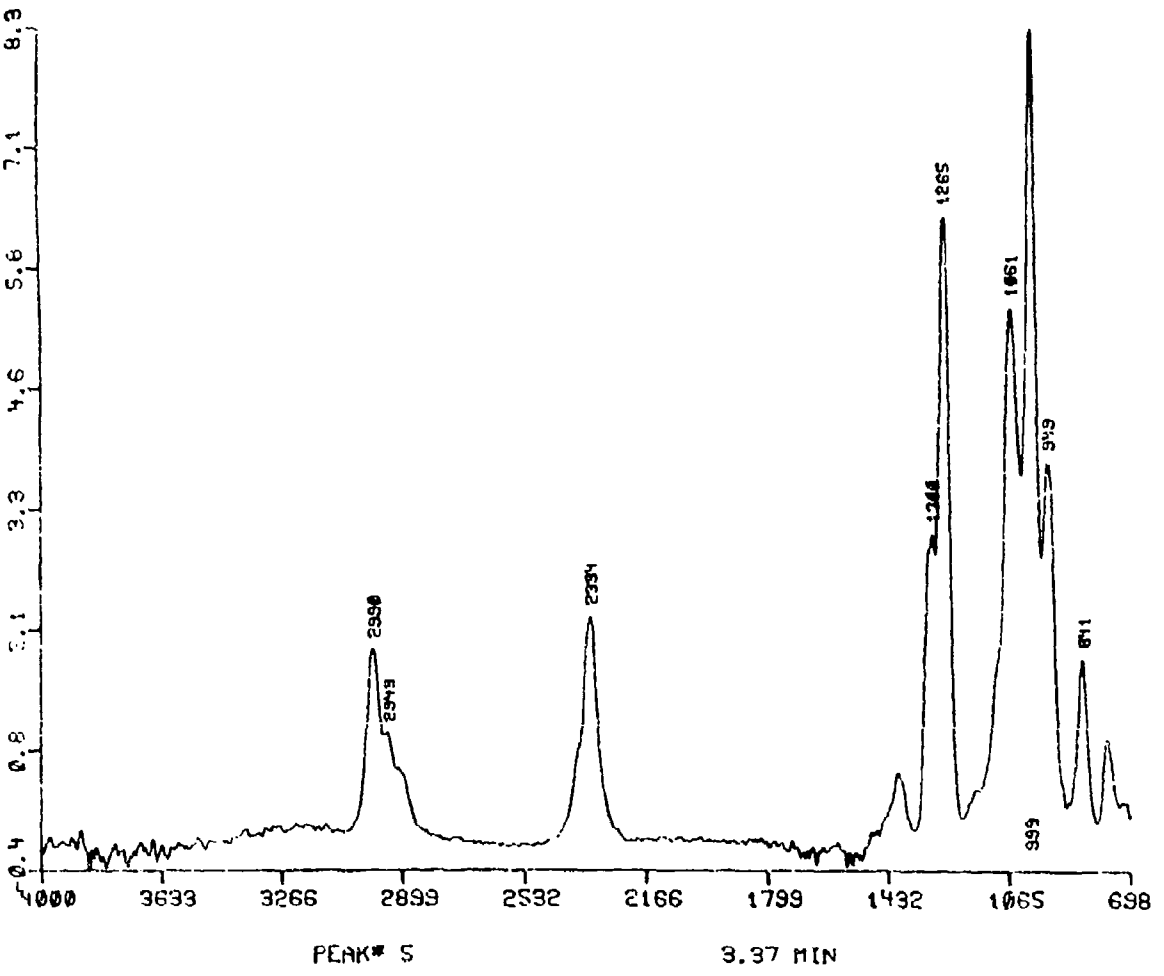


Figure 52. Peak No. 5 Unknown

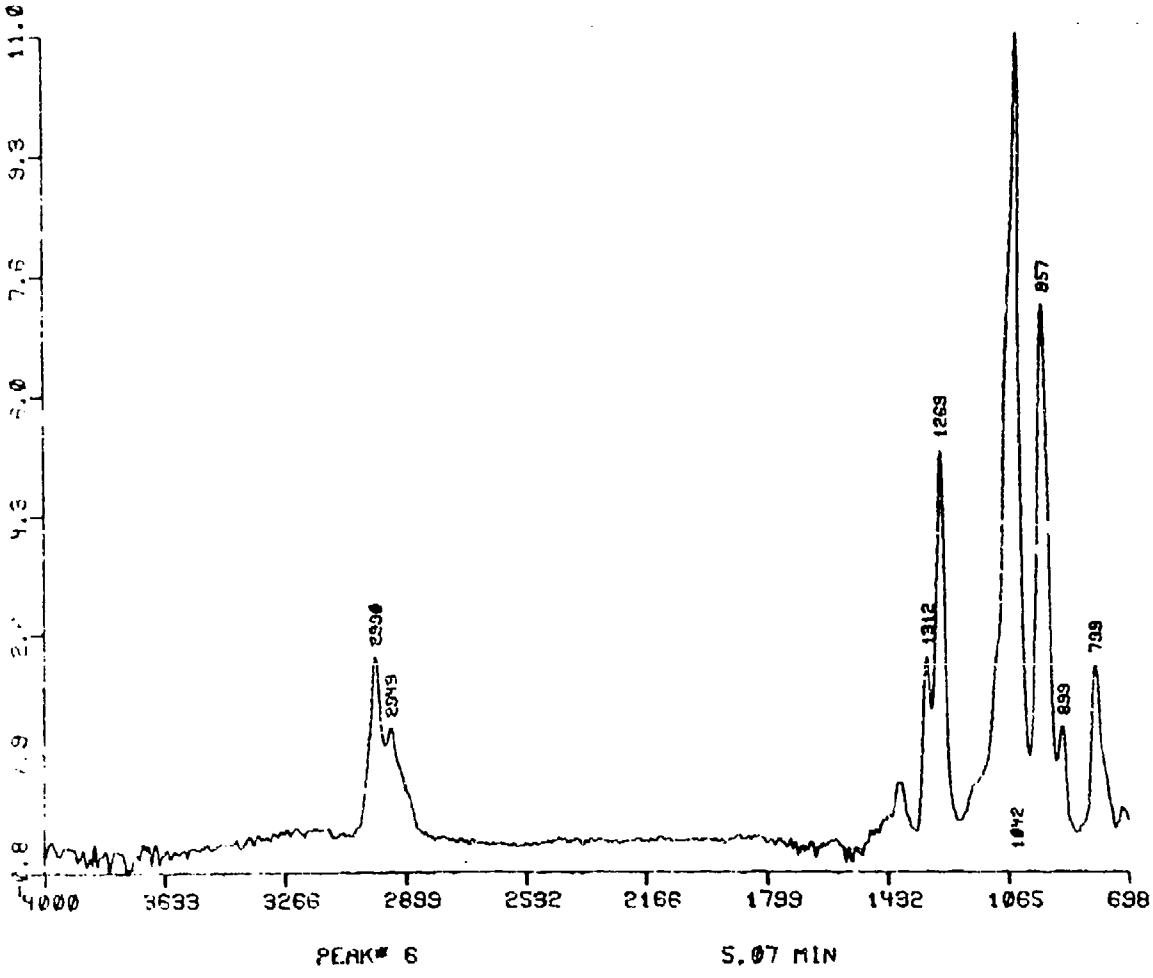


Figure 53. Peak No. 6 YL

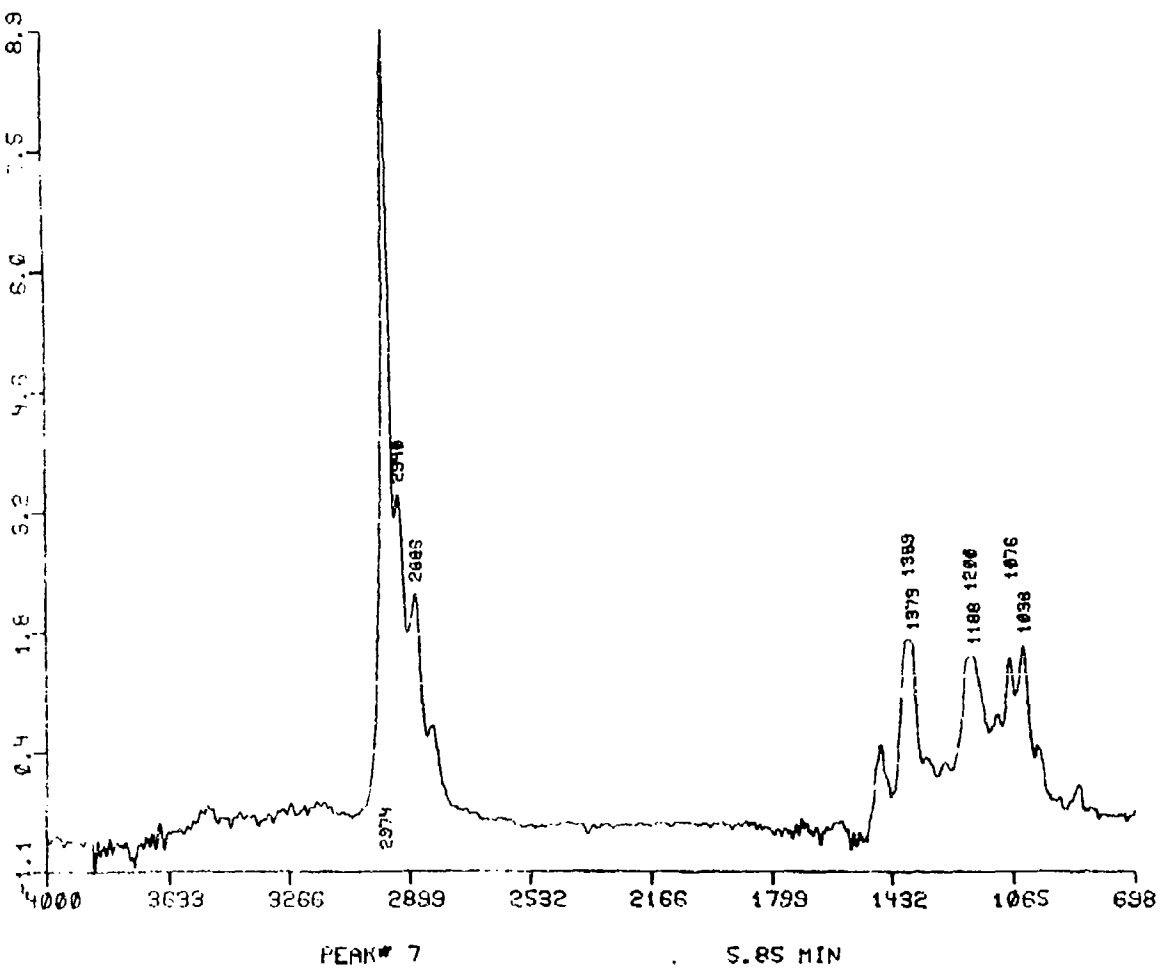


Figure 54. Peak No. 7 KB

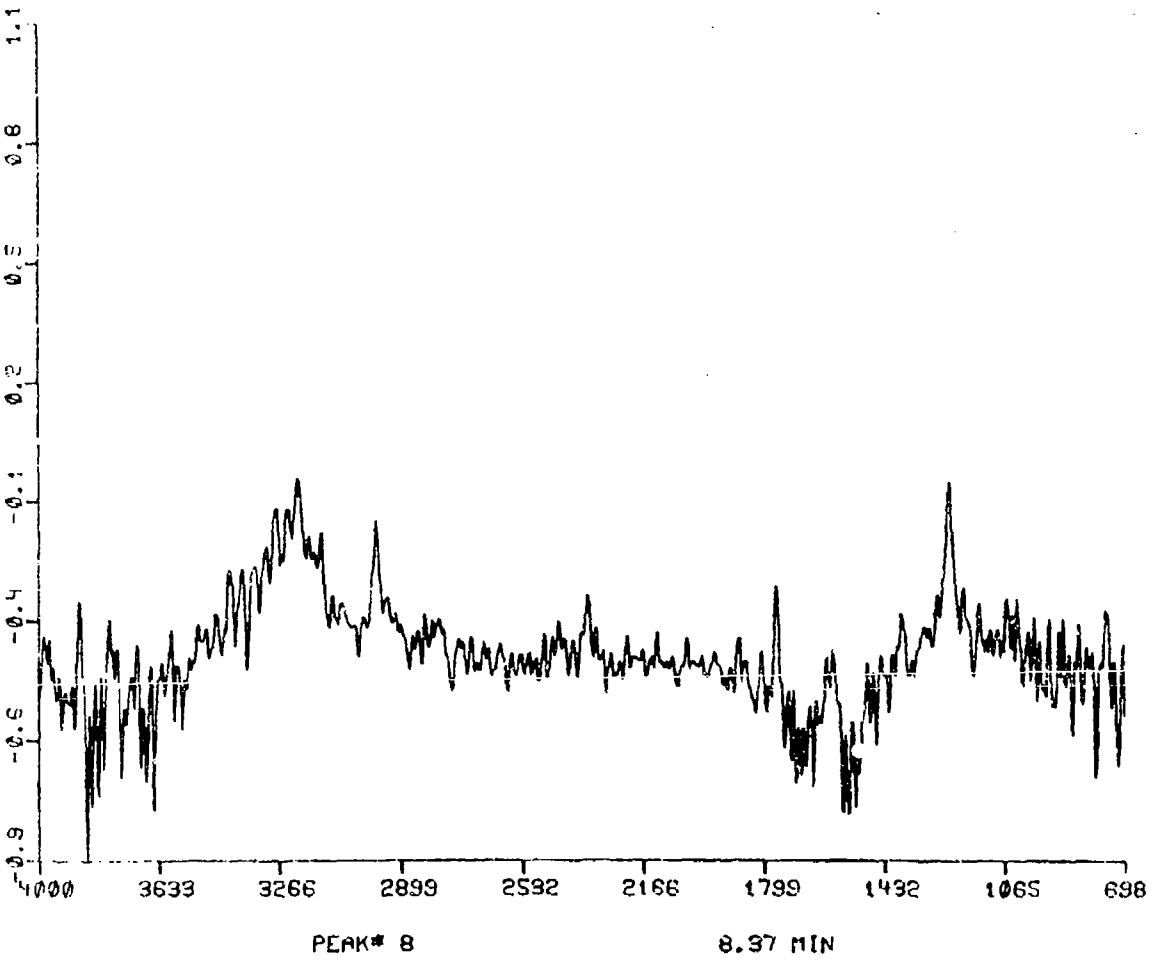


Figure 55. Peak No. 8 Unknown

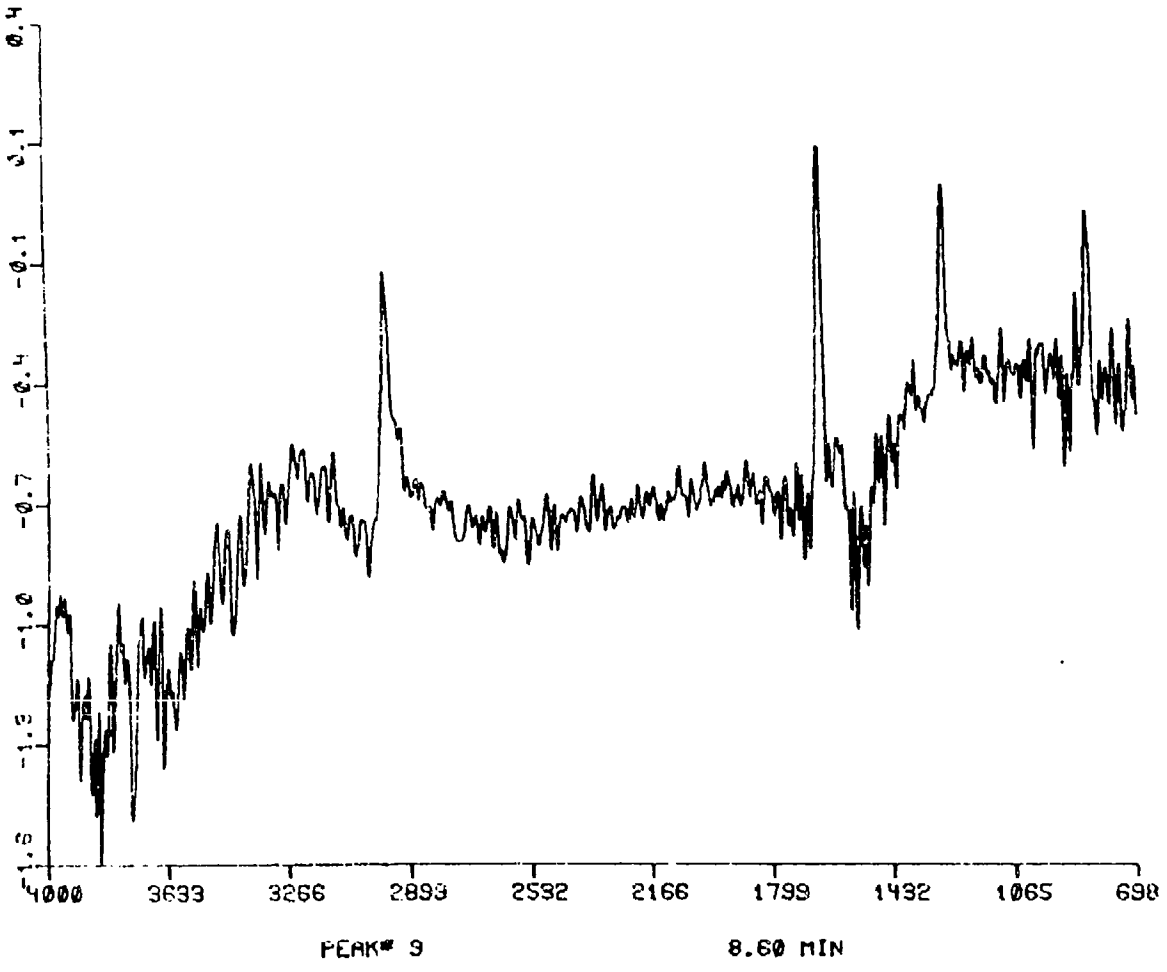


Figure 56. Peak No. 9 TEP

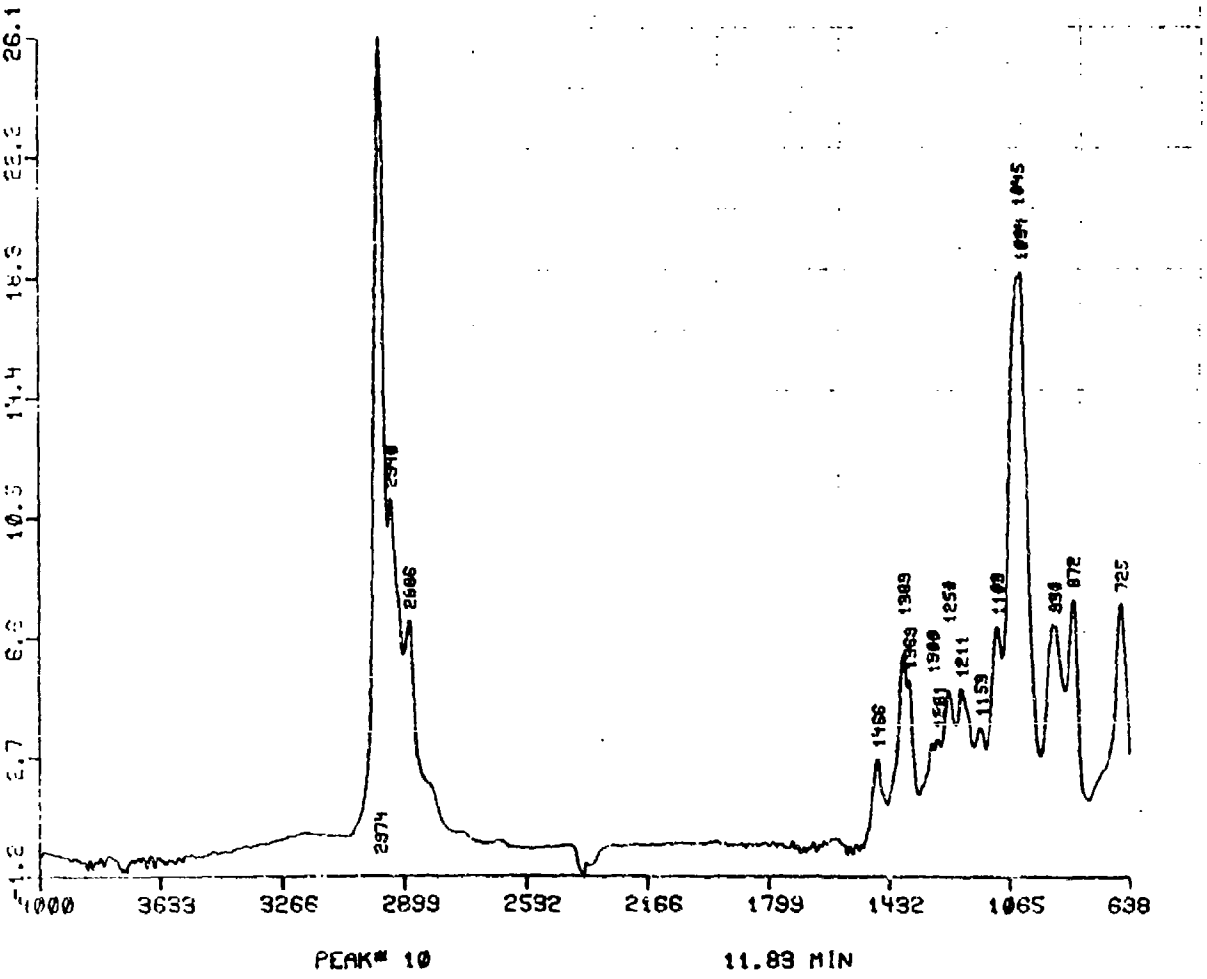


Figure 57. Peak No. 10 QL

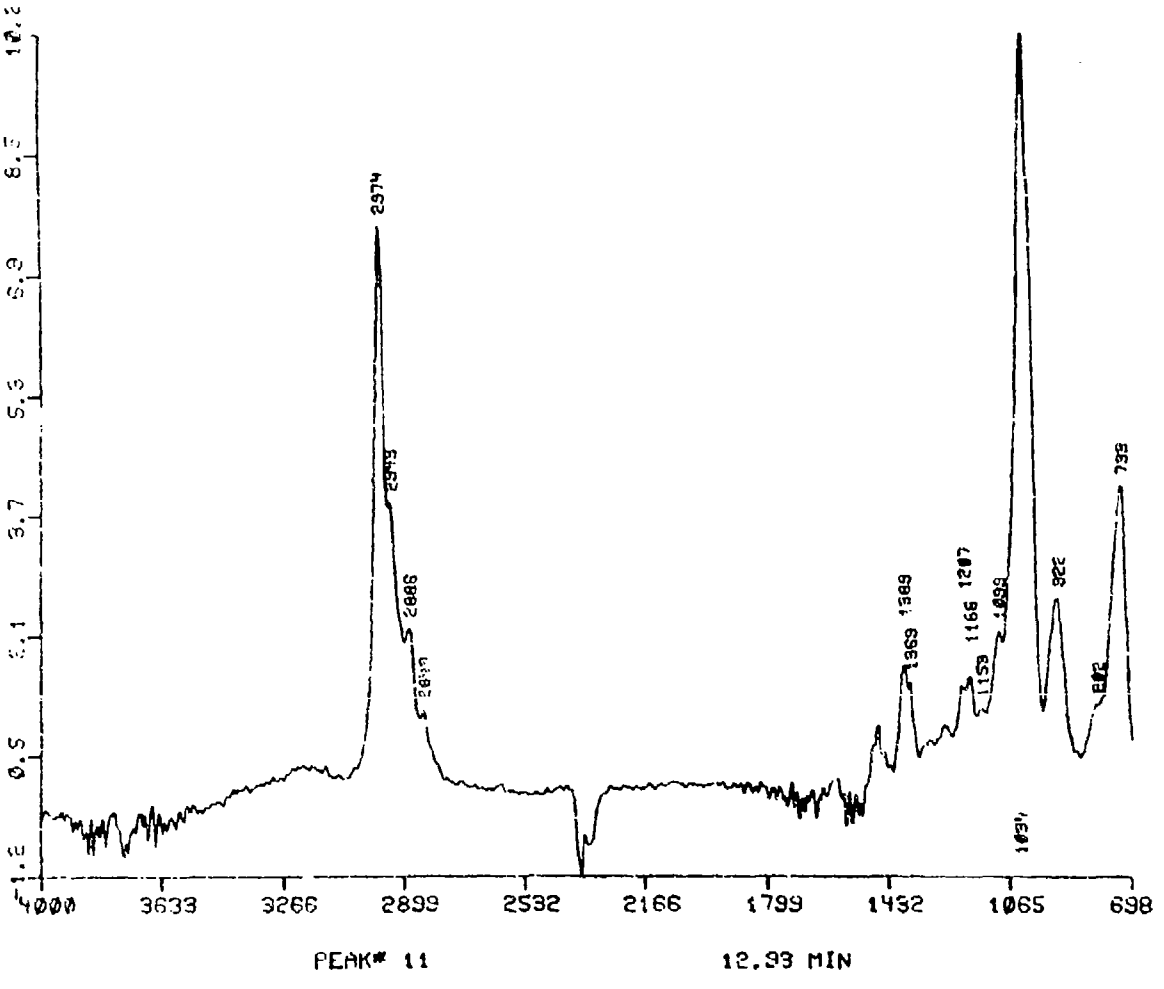


Figure 58. Peak No. 11 QA

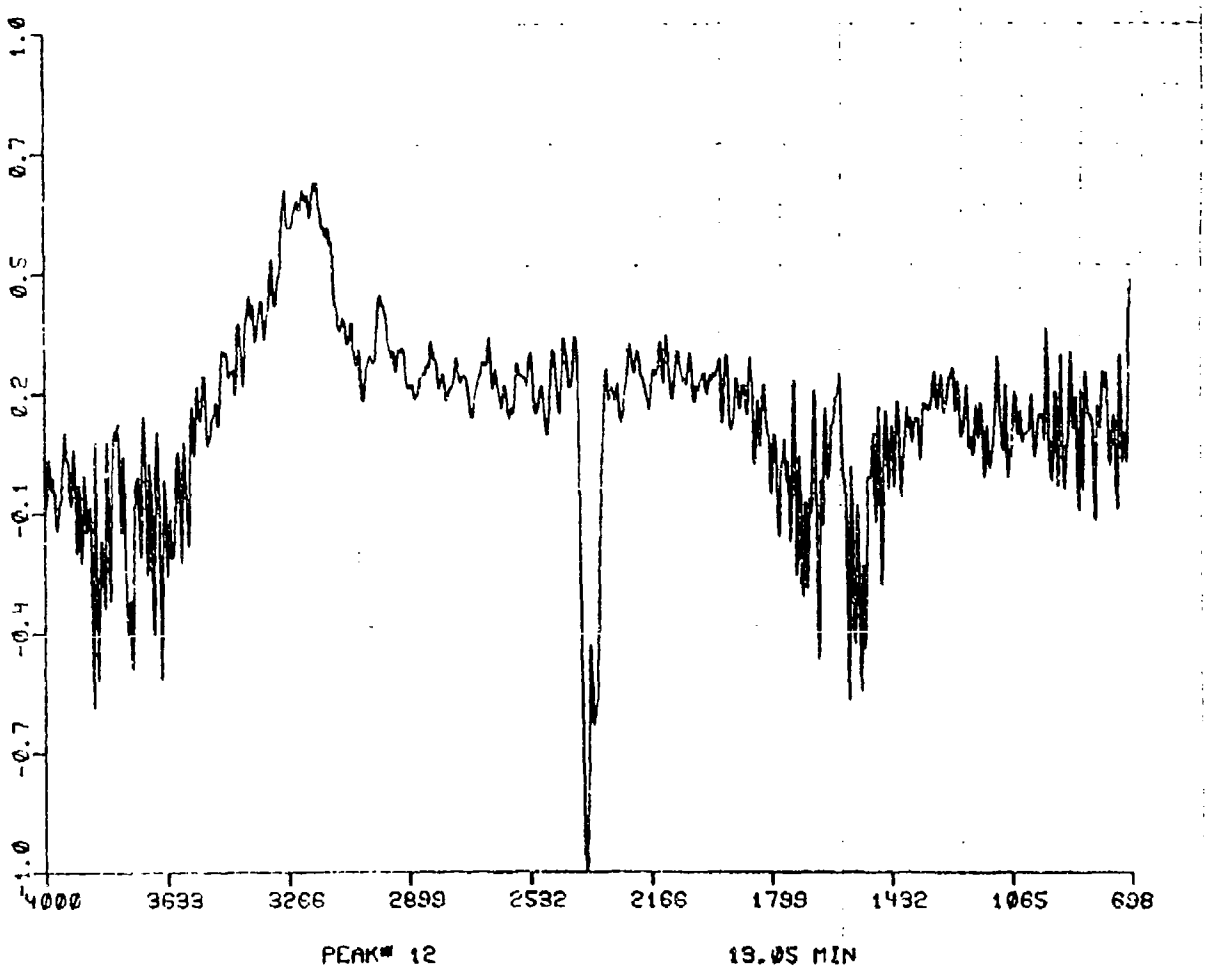


Figure 59. Peak No. 12 Unknown

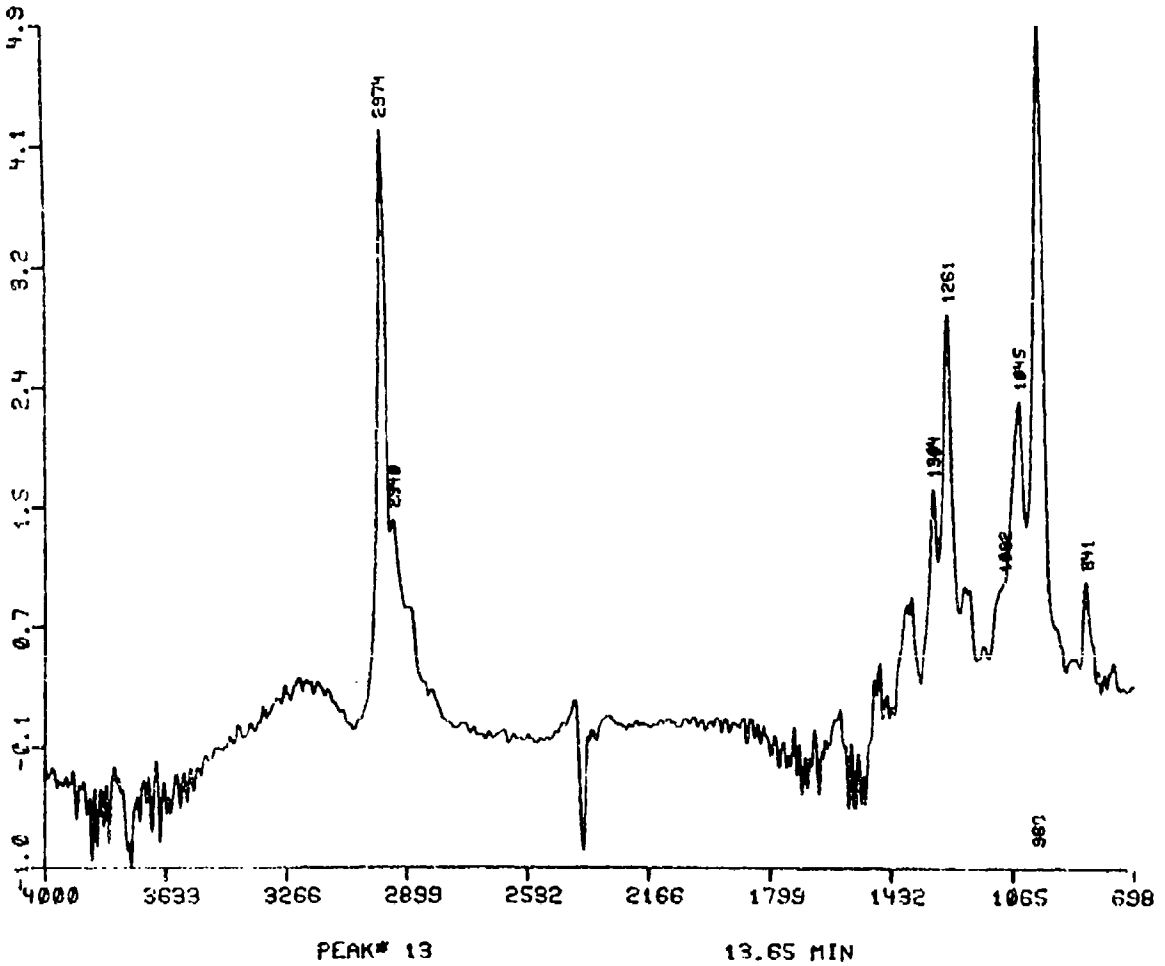


Figure 60. Peak No. 13 QB

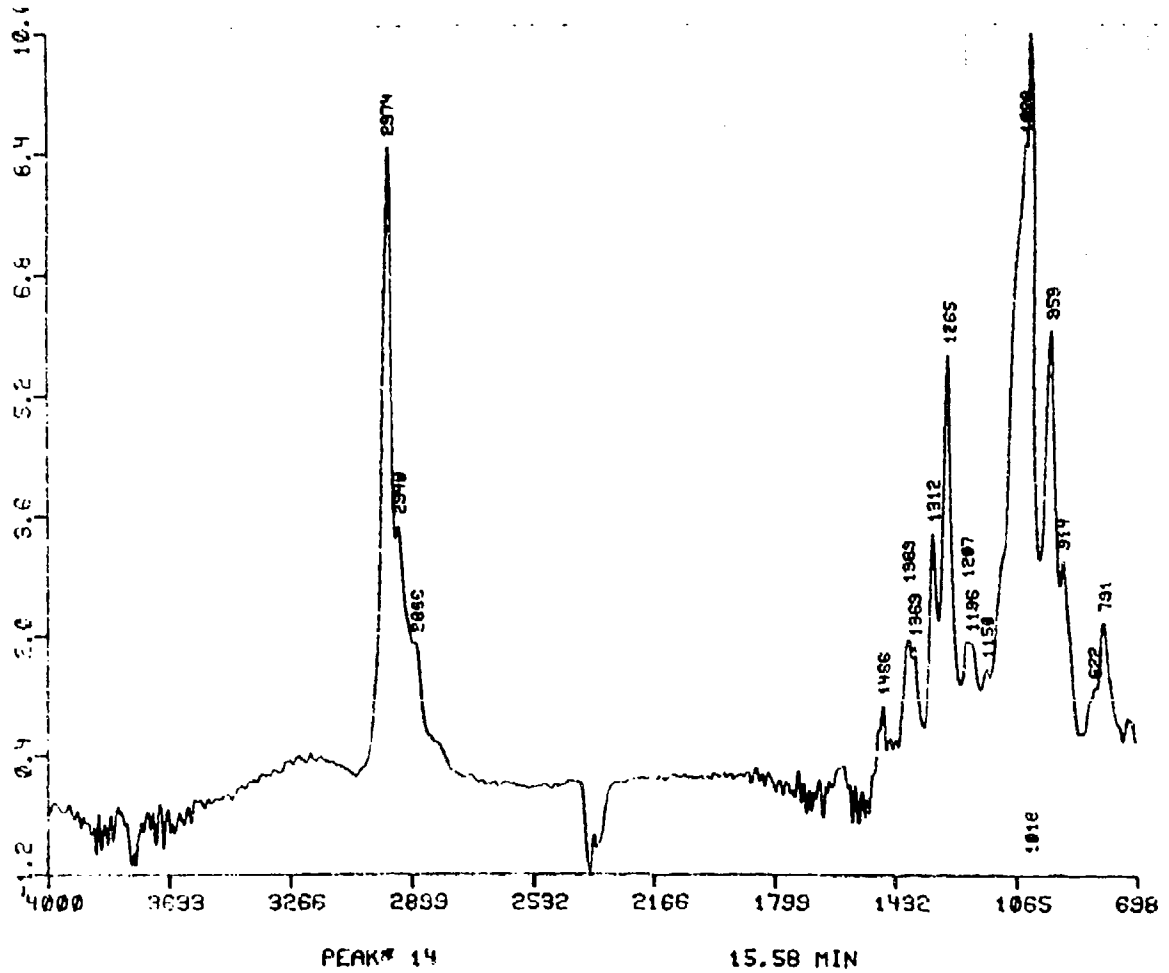


Figure 61. Peak No. 14 QC

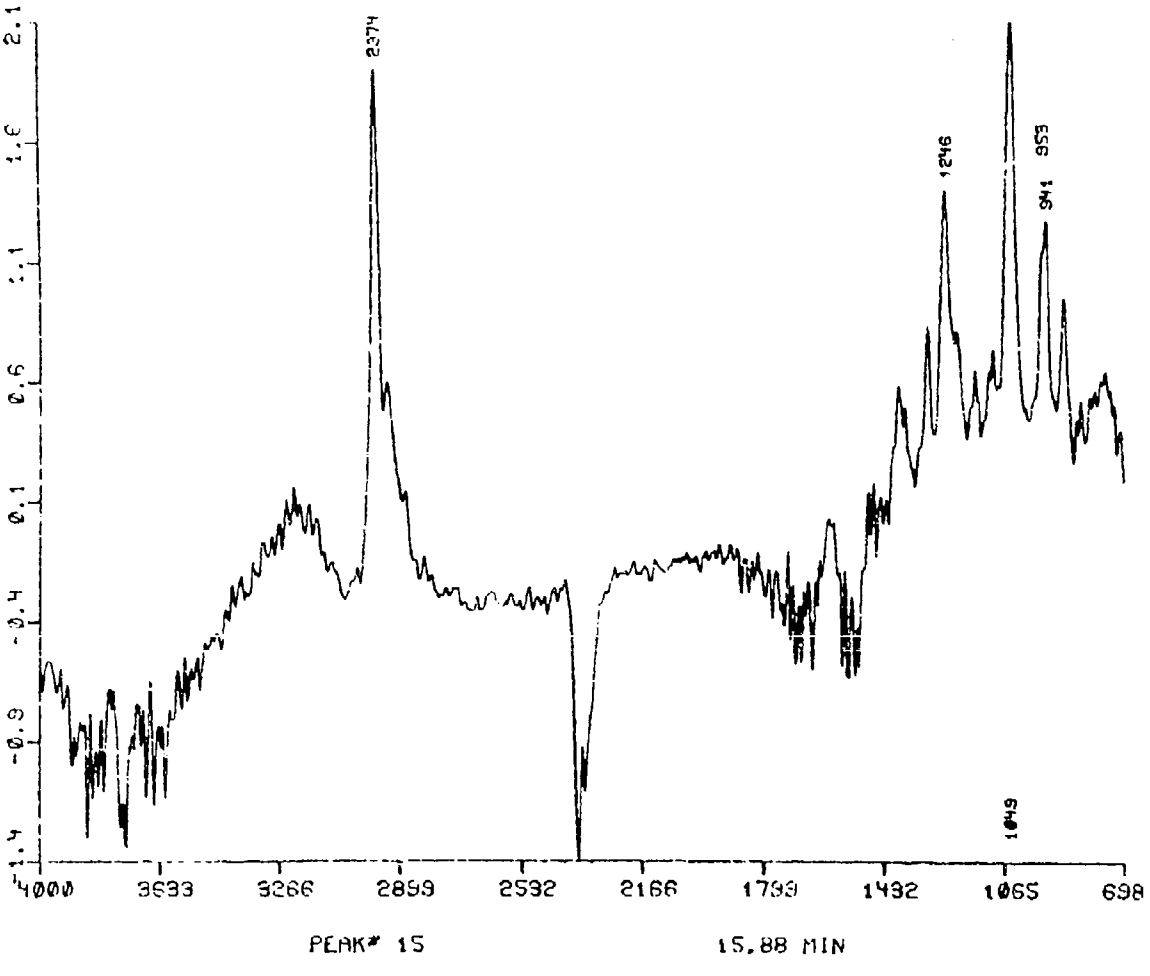


Figure 62. Peak No. 15 QD

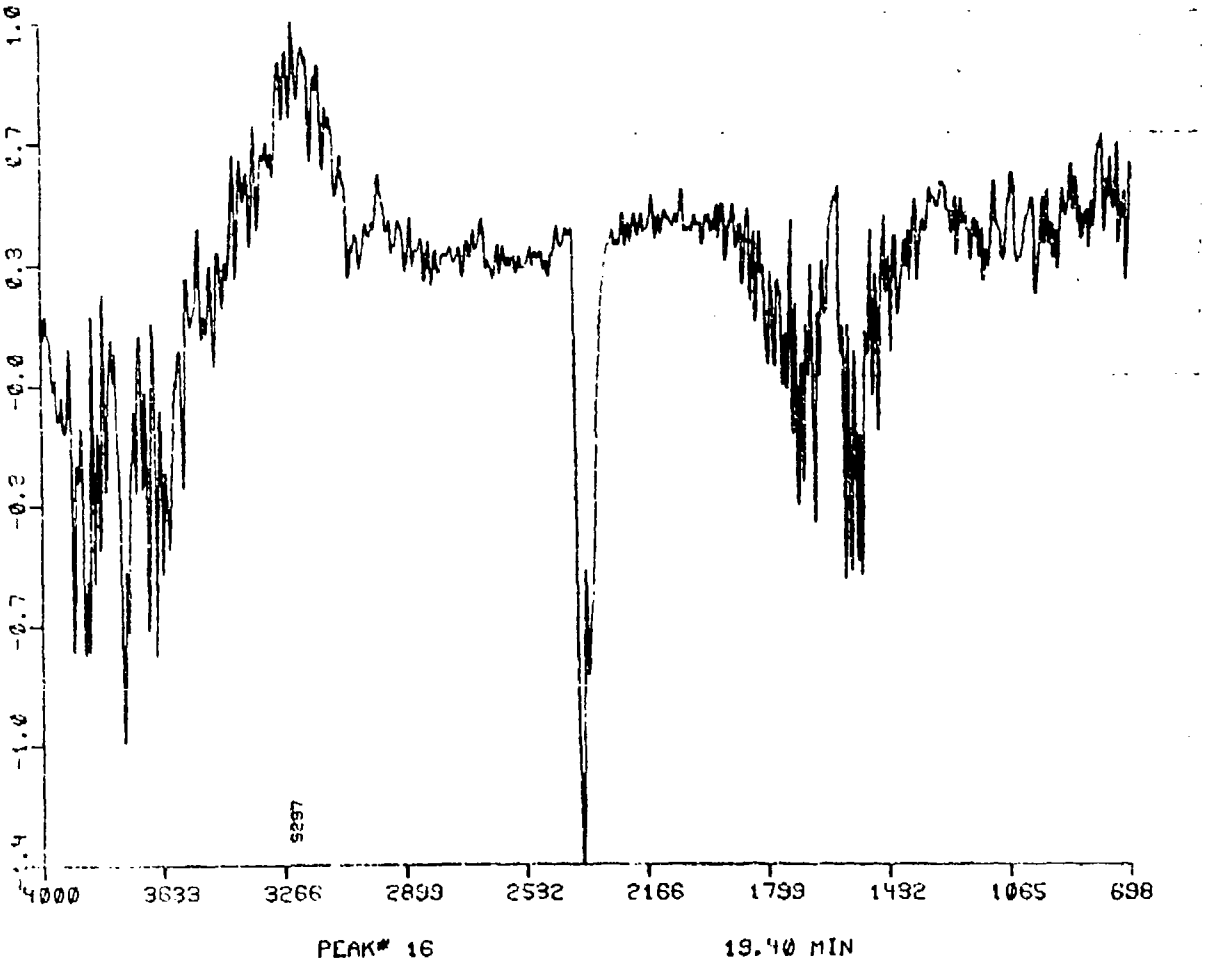


Figure 63. Peak No. 16 Unknown

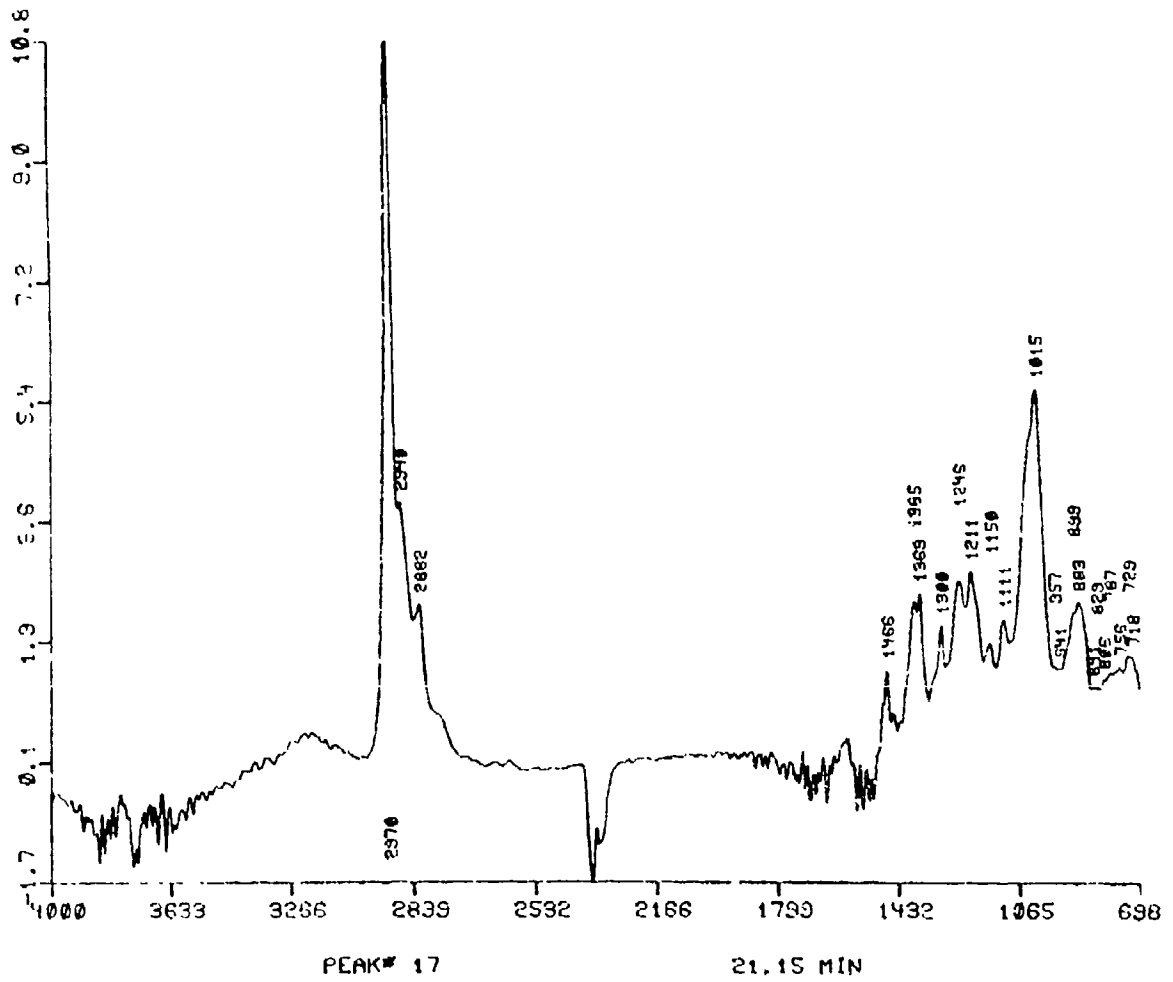


Figure 64. Peak No. 17 LT

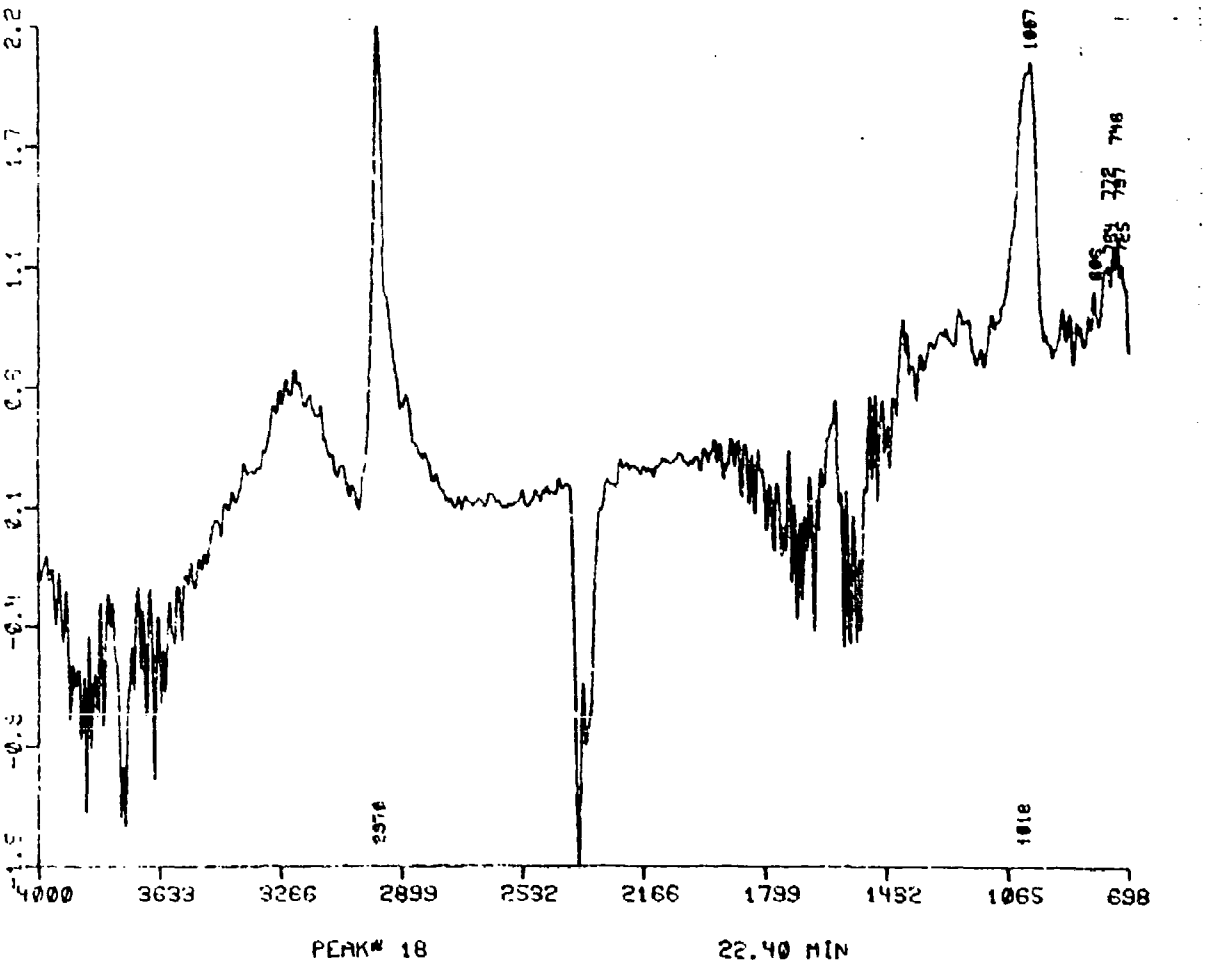


Figure 65. Peak No. 18 Unknown

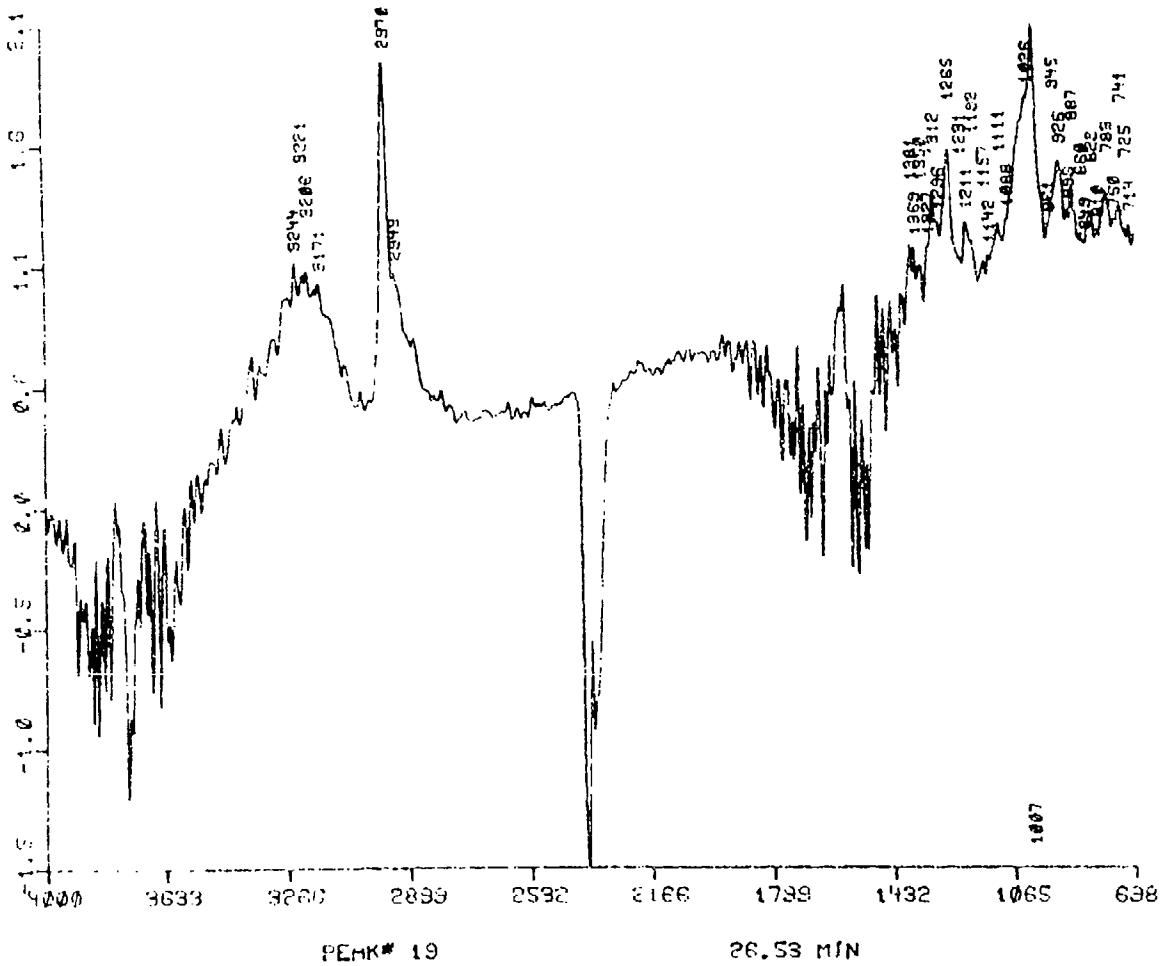


Figure 66. Peak No. 19 Unknown

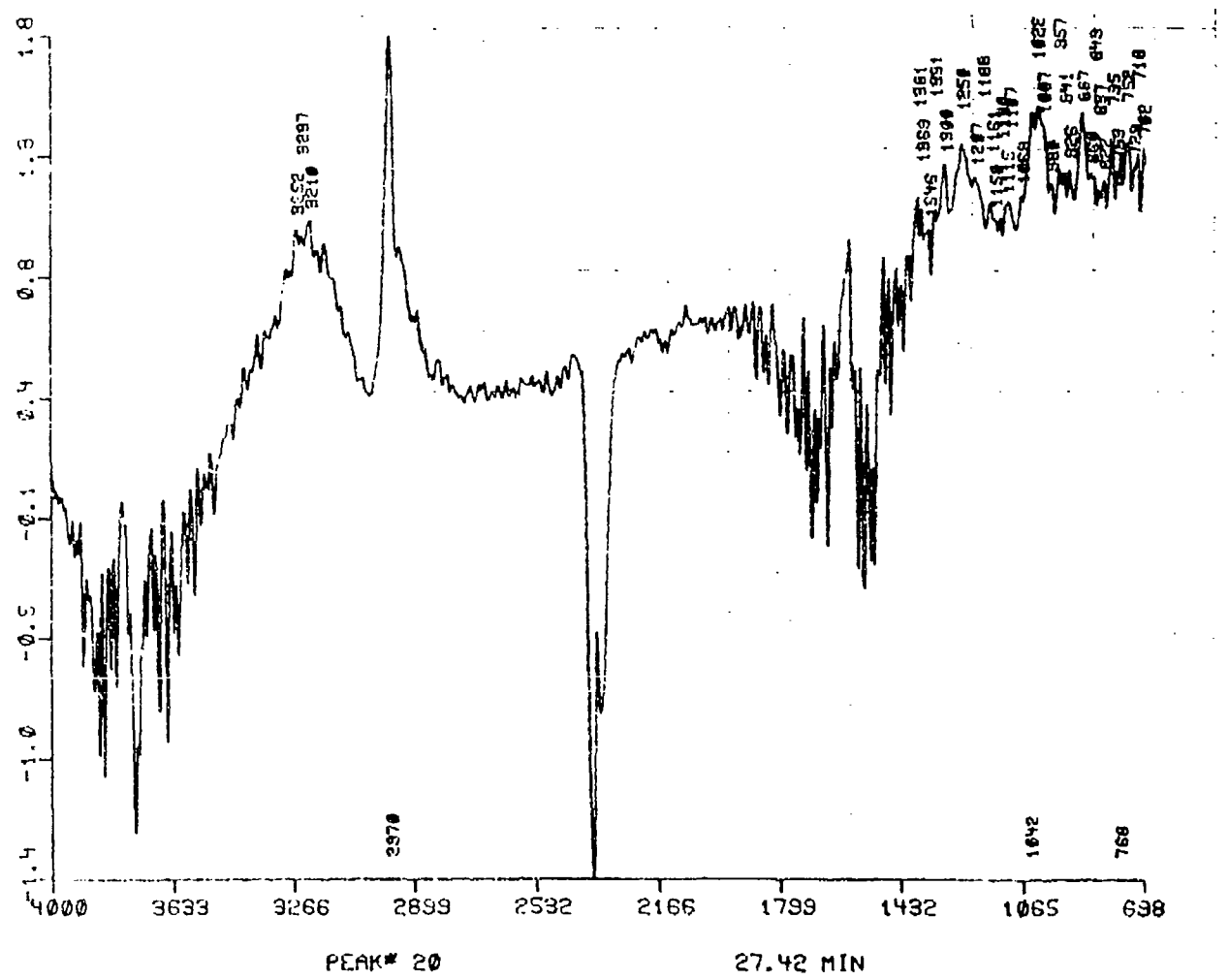


Figure 67. Peak No. 20 Unknown

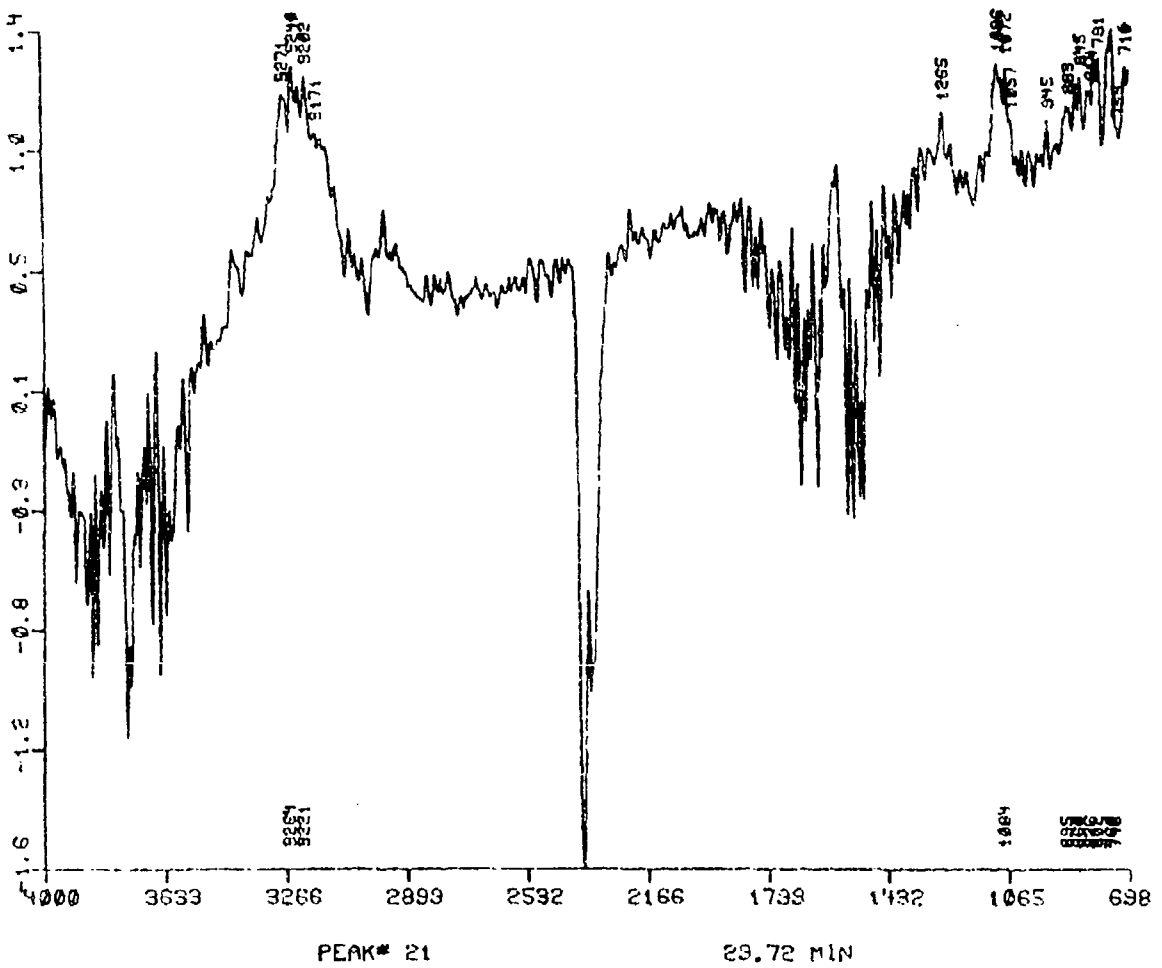


Figure 68. Peak No. 21 Unknown

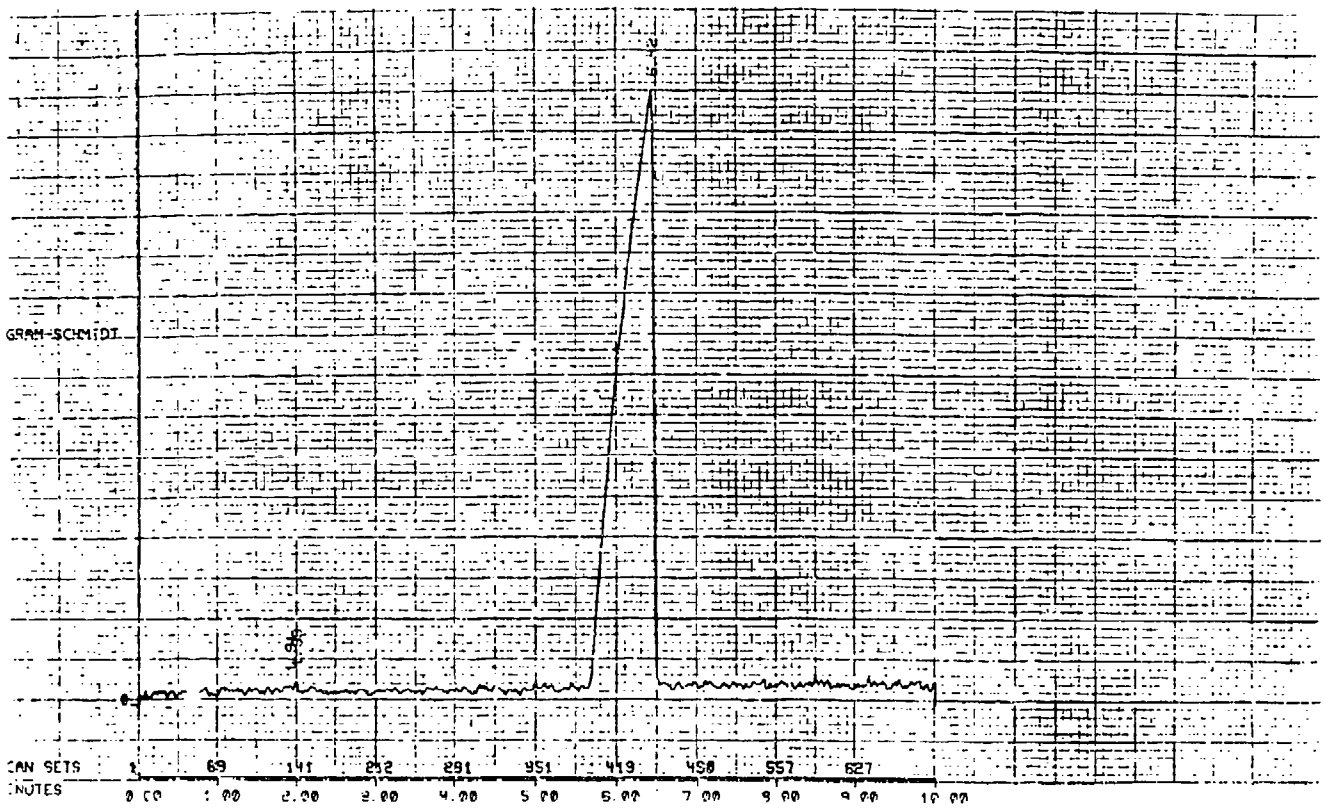


Figure 69. Gram-Schmidt for KB

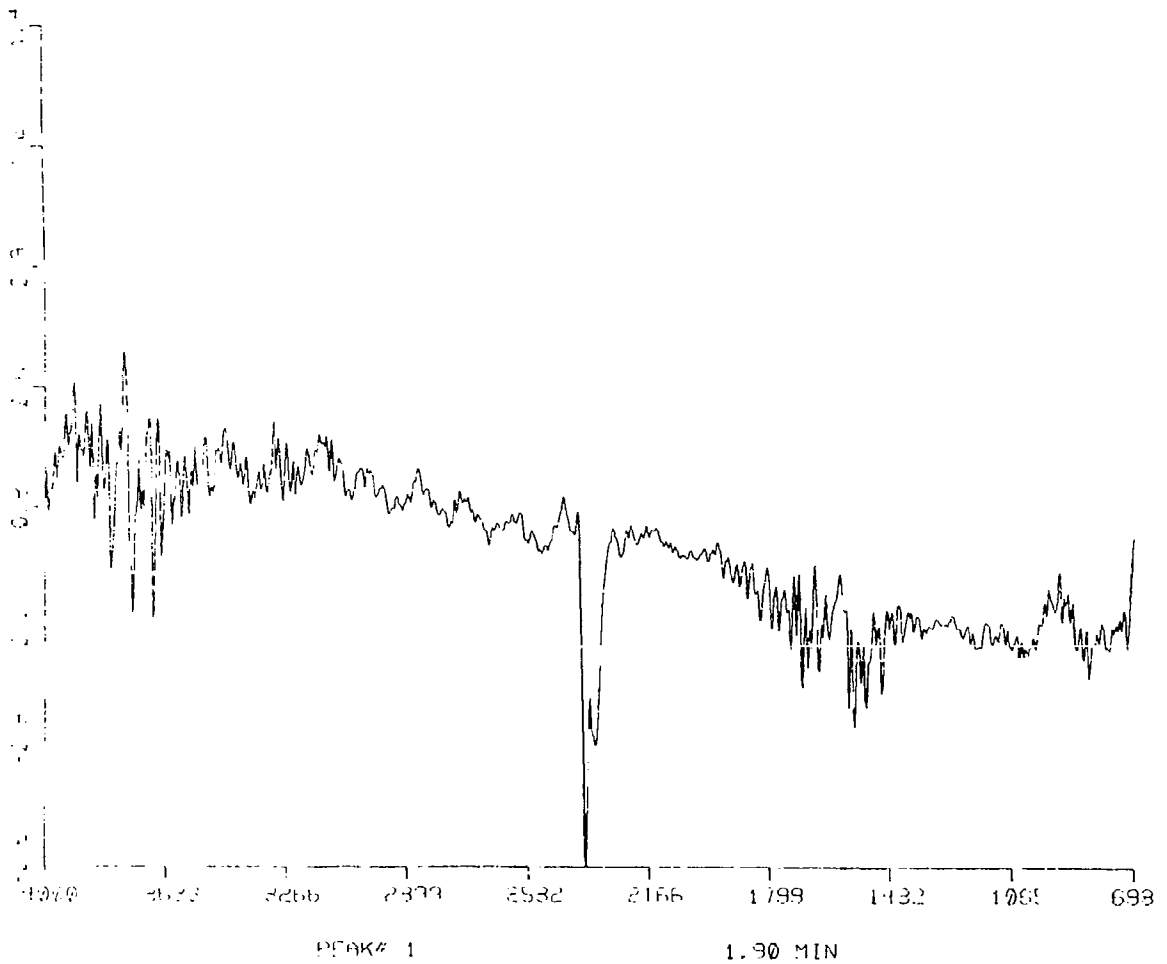


Figure 70. Peak No. 22 Unknown

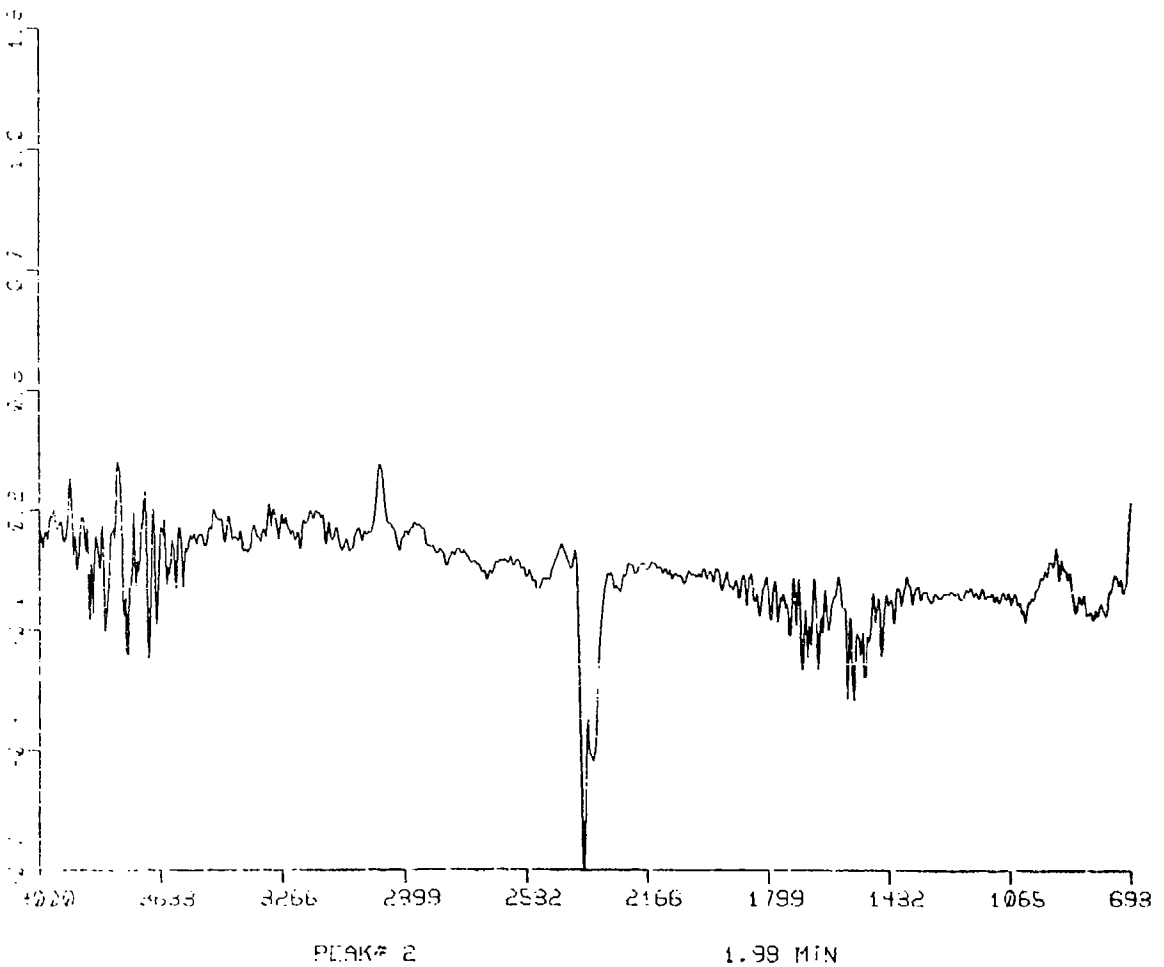


Figure 71. Peak No. 23 Unknown

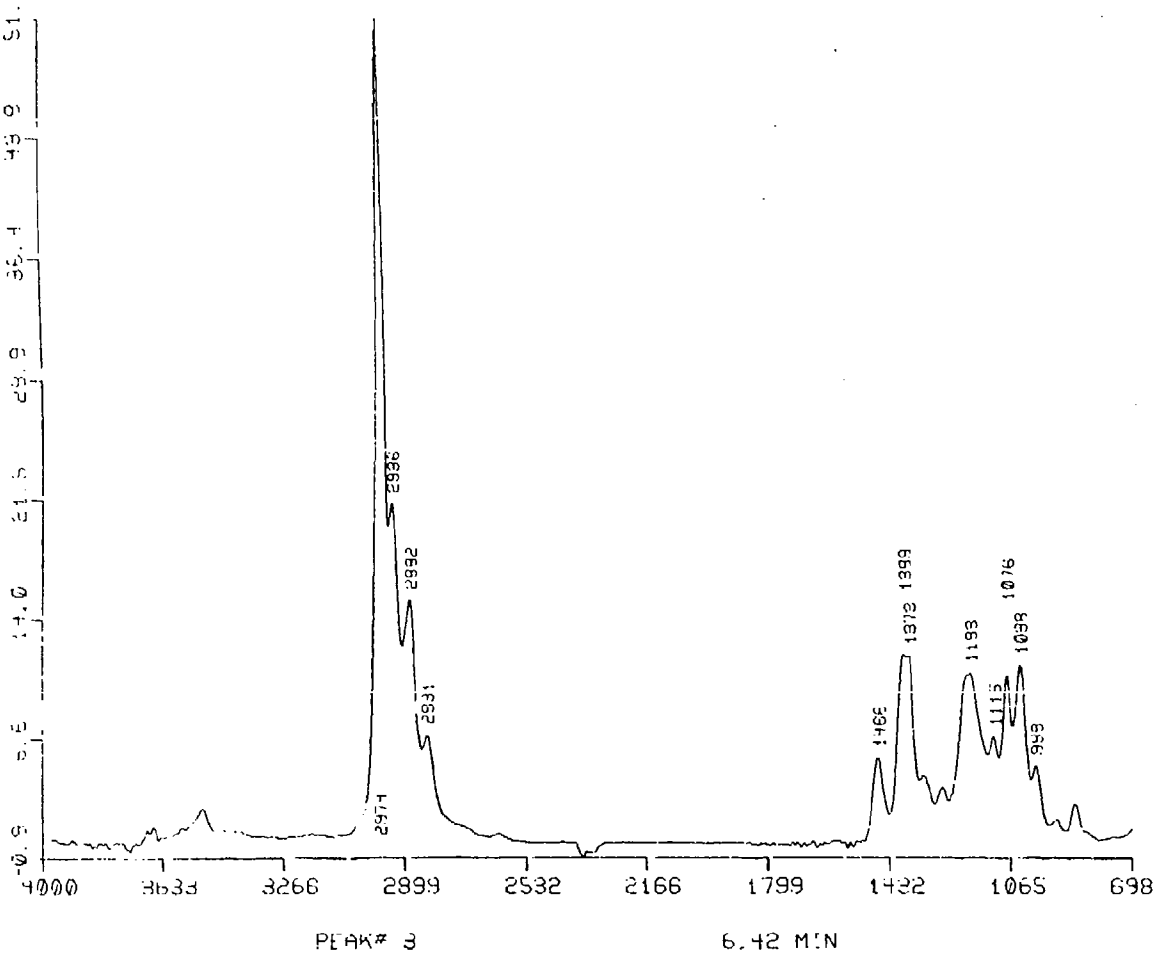


Figure 72. Peak No. 24 KB

sets/minutes. This corresponds to the columns appearing on the peak tables (Tables 23 and 24). Peak number identifies the individual FTIR spectrum.

The time (minutes) and scan sets columns in the peak tables identify the precise location on the Gram-Schmidt spectrum where the individual peaks are located.

Mid time and sets give the central point of the peak number in question (the center of the range for the FTIR Spectrum). Status of the FTIR indicates if the data collected are raw data or analyzed data. By assessing the data, the experimenter is sure a representative sample of the peak in question has been obtained. Once the data are examined, the peak's status becomes identified. Identical FTIR regions were combined for a specific peak. This was especially critical when a peak was labeled as a possible mixture. Smaller and smaller scan sets are viewed with hopes of isolating the mixture if it exists. In our case, the possible mixtures could not be assessed as mixtures. The FTIR spectrum of the KB component of hydrolyzed QL compared with the pure sample without any deviation. The units for the GC-FTIR spectra are wavenumber (x-axis) versus intensity (y-axis).

Table 23. Peak Table for Correlating Gram-Schmidt and FTIR Spectrum (QL)

Peak No.	Components	Time (min)	Scan Sets	Mid Time	Sets	Status
1	EtOH	1.69-1.72	122-124	1.70	123	Reduced
2	TR	2.62-2.68	186-190	2.65	188	Reduced
3	Unknown	2.74-2.80	194-198	2.74	194	Reduced
4	Unknown	3.18-3.22	225-228	3.20	227	Reduced
5	Unknown	3.34-3.40	236-241	3.37	239	Reduced, Possible Mixture
6	YL	5.02-5.10	354-359	5.07	357	Reduced
7	KB	5.79-5.89	407-413	5.95	411	Reduced, Possible Mixture
8	Unknown	8.37-8.38	587-588	8.37	587	Reduced
9	TEP	8.61-8.62	604-605	8.61	604	Reduced
10	QL	11.64-11.89	816-834	11.85	831	Reduced, Possible Mixture
11	OA	12.88-12.95	906-911	12.93	910	Reduced
12	Unknown	13.05-13.06	918-919	13.05	918	Reduced

Table 23. Peak Table for Correlating Gram-Schmidt and FTIR Spectrum (QL) (Continued)

Peak No.	Components	Time (min)	Scan Sets	Mid Time	Sets	Status
13	QB	13.59-13.69	957-964	13.66	962	Reduced
14	QC	15.48-15.62	1093-1103	15.58	1100	Reduced, Possible Mixture
15	QD	15.87-15.91	1121-1124	15.88	1122	Reduced
16	Unknown	19.41-19.42	1373-1374	19.41	1373	Reduced
17	LT	21.03-21.20	1484-1495	21.15	1492	Reduced, Possible Mixture
18	LTO	22.39-22.44	1576-1580	22.41	1578	Reduced
19	Unknown	26.51-26.59	1863-1869	26.53	1865	Reduced
20	Unknown	27.39-27.44	1930-1934	27.43	1933	Reduced
21	Unknown	29.72-29.74	2106-2108	29.74	2107	Reduced

Table 24. Peak Table for Correlating Gram-Schmidt and FTIR Spectrum (Pure KB)

Peak No.	Component	Time (min)	Scan Sets	Mid Time	Sets	Status
1	Unknown	1.91-1.93	135-136	1.91	135	Reduced
2	Unknown	1.80-2.11	127-150	1.99	141	Reduced
3	KB	5.98-6.45	410-415	6.42	449	Reduced

4.7 MIRAN 80 Reproducibility.

There are several ways to establish reproducibility and accuracy. In this case, they are dependent on the MIRAN 80's ability to monitor a known concentration with time and record the absorbance value. The simplest method for determining reproducibility is to repeatedly analyze a known compound at the appropriate wavelength over time.

This method was not used because the MIRAN 80 in this assessment was required to analyze KB and YL at 6 wavelengths (see Table 25), which

spanned the region of 4.00-11.2 μm. The approach taken involved repeated calibration using the liquid injection calibration technique described in section 4.3. The MIRAN 80 was recalibrated six times for the components KB and YL. In so doing, the accuracy of the servo motor was incorporated into the results presented in data Tables 25-31. From the repeated values measured for each calibration run for both KB and YL at a given wavelength, the servo motor turns the filter wheel to a specific position and provides an IR response to the component trapped in the IR cell. By selecting a concentration and its absorbance value for KB wavelength (8.44, 8.528, 8.543, and 8.826 μm) or YL wavelengths (10.45 and 11.20 μm) and Comparing them to another trial, the reproducibility of the MIRAN is illustrated. A large error of measurement is obtained when injecting the first aliquot of either component. This is drastically illustrated by the large discrepancy in values obtained in trial 3, wavelength 8.44, as compared to trials 2 and 4 of the same wavelength. Although the values do not agree exactly, a linear response is indicated when the data for a given wavelength is plotted. The linearity and reproducibility are graphically illustrated. If another calibration method could be derived that would eliminate the error in measuring 0.2 μL, the deviation in measured absorbance value would not exist. The data collected represent three point calibration curves (three presented concentrations) for two components using six wavelengths. Six calibration curves are presented in Figures 73 and 74. Figures 75-78 represent the least squares fit with 95% confidence interval of the same data with supporting numerical values. Figures 75 and 76 illustrate the linearity and relative reproducibility obtained by the liquid injection technique. The equations for the curve and coefficient of determination are the most important values. The coefficient of determination indicates data reliability. The closer to a value of 1, the better the data (i.e., plotted curve point).

Table 25. Concentration Matrix (Trials 1-6)

			3 Points 6 Wavelengths 2 Components			
Component	Parts-Per-Million				$(1*10^{-6})$ = ppm	
Sample 1, KB	0.52	0.52	0.52	0.52	0	0
	1.56	1.56	1.56	1.56	0	0
	2.60	2.60	2.60	2.60	0	0
Sample 2, YL	0	0	0	0	0.425	0.425
	0	0	0	0	1.275	1.275
	0	0	0	0	2.215	2.215

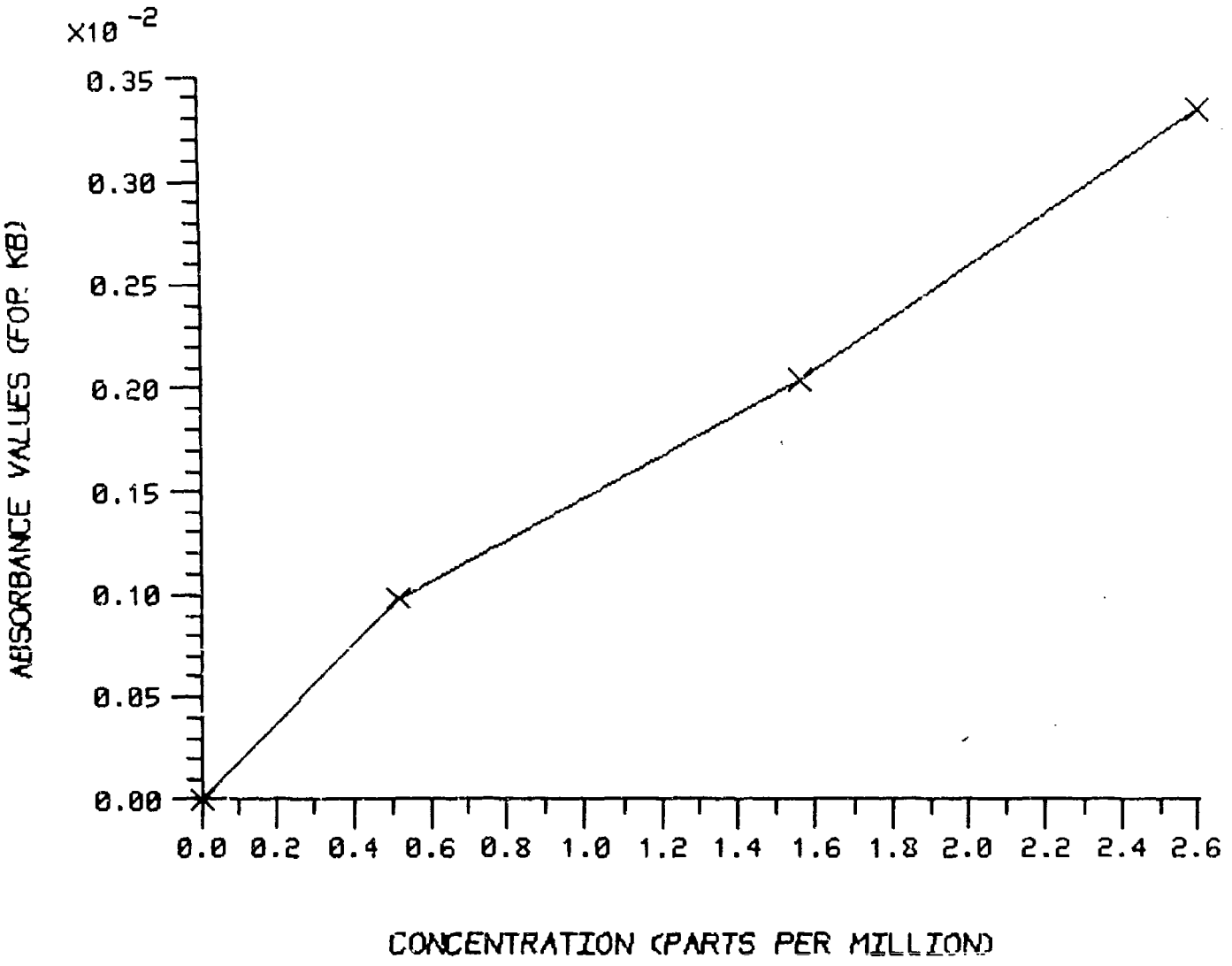


Figure 73. Average of Six Trial Runs for KB at 8.543 μm

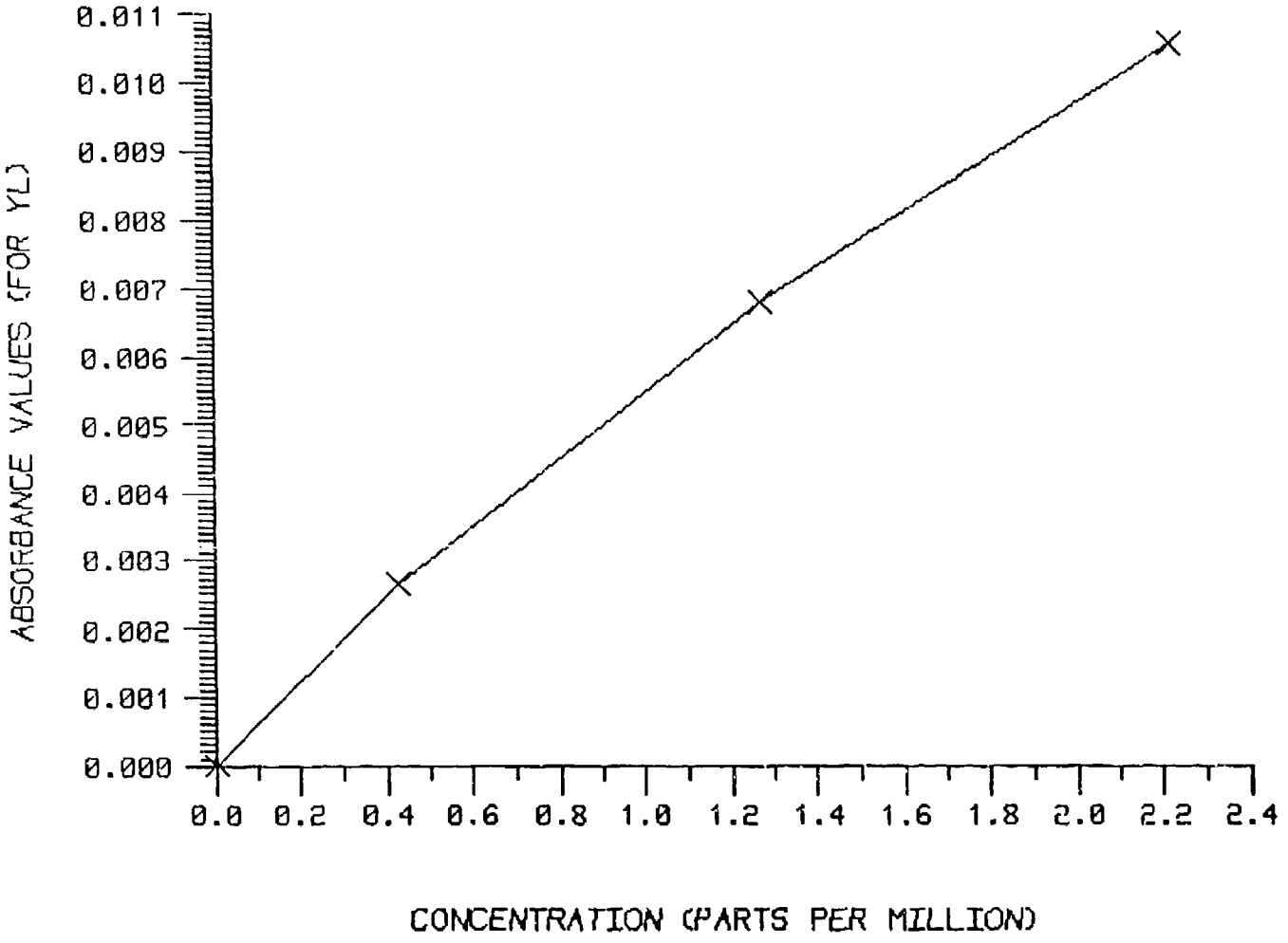


Figure 74. Average of Six Trial Runs for YL at 10.45 μm

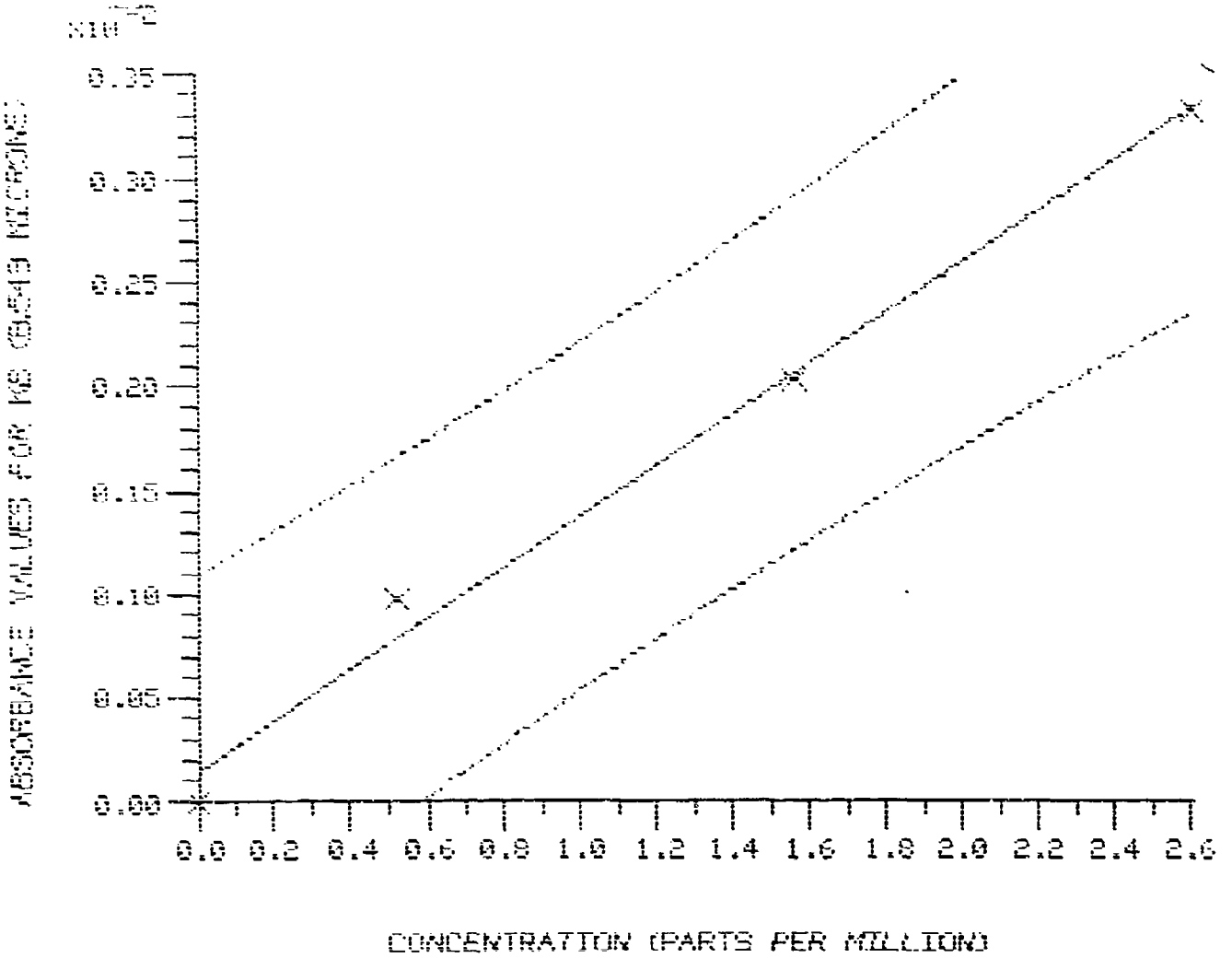


Figure 75. Calibration Curve for Average KB Runs with 95% Confidence Lines

```
DATA SET NO.  2                    MIRAN.AVG1(0)

X MEAN =       1.17000             X STD.DEV.=       1.15303
Y MEAN =     1.585000-03           Y STD.DEV.=     1.428437-03


 Y= 1.427I-04+1.2327-03X**1
 ANAL.OF VAR.          DF    SUM OF SQUARES     MEAN SQUARE       STD. ERROR
 DUE TO REG.            1       6.060815-06       6.060815-06       2.461872-0
...3
 ERROR ABOUT REG.       2       6.040474-08       3.024237-08       1.739033-0
...4
 TOTAL                  3       6.121300-06
  F TEST:       200.408
  COEF.OF DETERMINATION:    .990119
```

Figure 76. Statistical Values for Figure 75

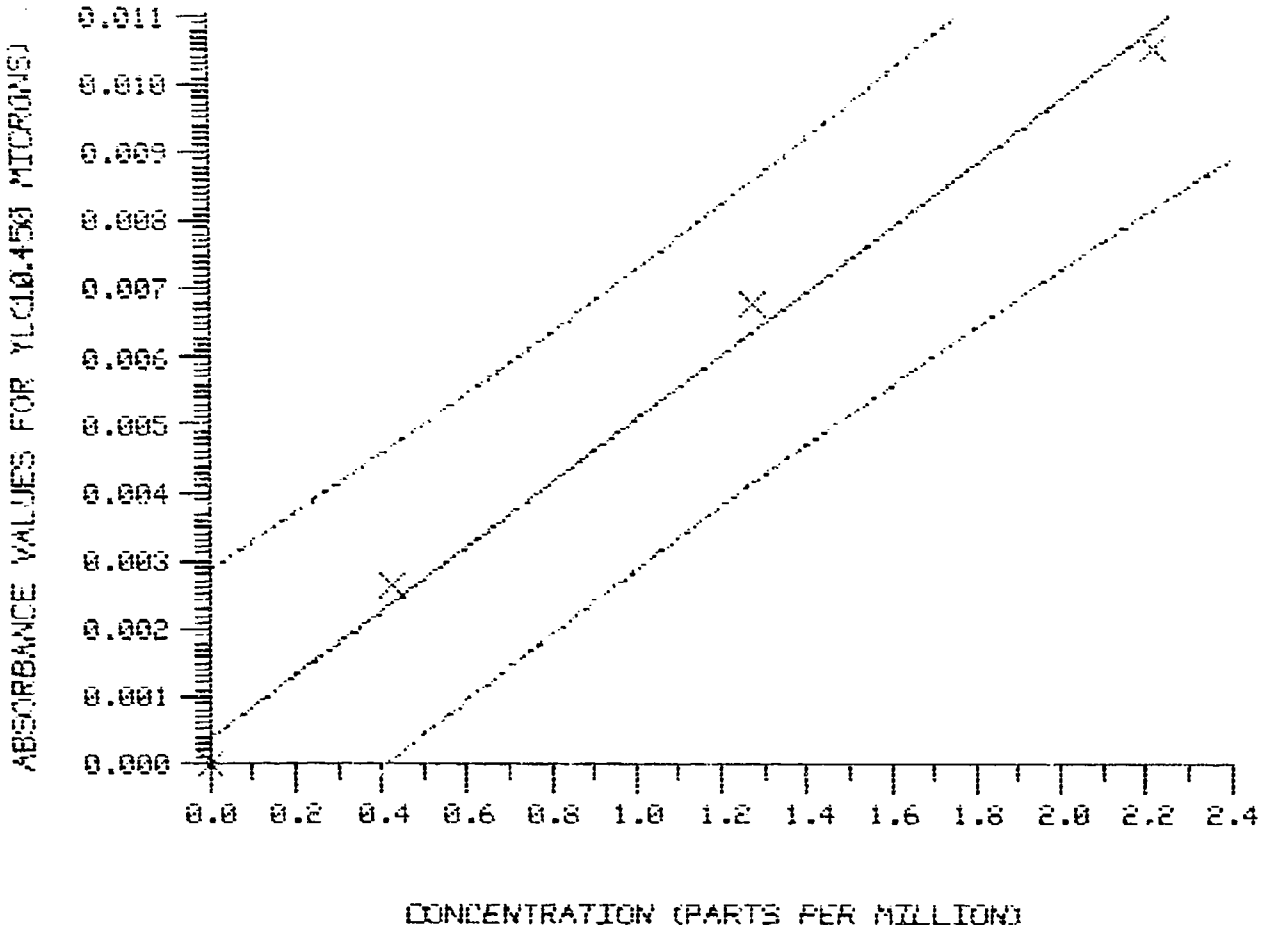


Figure 77. YL Calibration Curve with 95% Confidence Lines

```
DATA SET NO.  2                    AVERAGE(YL)

X MEAN =        .978750           X STD.DEV.=       .979910
Y MEAN =     4.987500-03          Y STD.DEV.=     4.638666-03


 Y= 3.6952-04+4.7102-03X**1
 ANAL.OF VAR.          DF    SUM OF SQUARES     MEAN SQUARE       STD. ERROR
 DUE TO REG.            1      6.412885-05       6.412885-05       0.000049-0
...3
 ERROR ABOUT REG.       2      4.228267-07       2.114134-07       4.597971-0
...4
 TOTAL                  3      6.455167-05
  F TEST:       303.334
  COEF.OF DETERMINATION:    .993450
```

Figure 78. Statistical Values for Figure 77

Table 26. Absorption Matrix, Trial 1

* 1*10-6				6 Wavelengths 2 Components 3 Points (Data)		
Wavelength*	8.440	8.528	8.543	8.826	10.450	11.200
Absorbtion Values for Samples 1-3, KB	.0008 .0018 .0027	.0010 .0025 .0035	.0008 .0025 .0037	.0006 .0026 .0041	.0008 .0017 .0021	.0005 .0009 .0009
Absorbtion Values for Samples 4-6, YL	.0010 .0019 .0031	.0003 .0005 0011	.0004 .0005 .0011	.0004 .0007 .0015	.0024 .0064 .0107	.0006 .0010 .0020

Table 27. Absorption Matrix, Trial 2

Wavelength*	8.440	8.528	8.543	8.826	10.450	11.200
Absorption Values for Samples 1-3, KB	.0013 .0018 .0025	.0012 .0019 .0033	.0013 .0020 .0034	.0010 .0018 .0033	.0005 .0008 .0012	.0006 .0007 .0009
Absorption Values for Sample 4-6, YL	.000 .0018 .0037	.000 .0007 .0019	.000 .0006 .0018	.0001 .0011 .0023	.0016 .0063 .0110	.0003 .0014 .0024

Table 28. Absorption Matrix, Trial 3

Wavelength*	8.440	8.528	8.543	8.825	10.450	11.200
Absorption Values for Samples 1-3, KB	.0003 .0012 .0019	.0003 .0010 .0022	.0002 .0013 .0025	.0002 .0011 .0025	.0004 .0007 .0010	.0004 .0005 .0008
Absorption Values for Samples 4-6, YL	.0012 .0031 .0051	.0010 .0017 .0030	.0010 .0018 .0028	.0006 .0015 .0026	.0018 .0065 .0112	.0008 .0017 .0026

Table 29. Absorption Matrix, Trial 4

Wavelengths*	8.440	8.528	8.543	8.826	10.540	11.200
Absorption	.0009	.0009	.0009	.0006	.0003	.0006
Data	.0014	.0017	.0017	.0014	.0005	.0007
Samples	.0022	.0027	.0028	.0023	.0009	.0009
1-3, KB						
Absorption	.0013	.0014	.0008	.0006	.0013	.0009
Values for	.0039	.0031	.0029	.0024	0058	.0021
Samples	.0056	.0037	.0035	.0032	.0110	.0029
4-6, YL						

Table 30. Absorption Matrix, Trial 5

Wavelength*	8.440	8.528	8.543	8.826	10.450	11.200
Absorption	.0015	.0013	.0014	.0011	.0010	.0009
Values for	.0021	.0023	.0023	.0022	.0010	.0009
Samples	.0031	.0037	.0041	.0036	.0018	.0015
1-3, KB						
Absorption	.0011	.0010	.0011	.0009	.0009	.0008
Values for	.0027	.0021	.0022	.0018	.0047	.0017
Samples	.0049	.0037	.0036	.0029	.0084	.0027
4-6, YL						

Table 31. Absorption Matrix, Trial 6

Wavelengths*	8.440	8.528	8.543	8.826	10.450	11.200
Absorption	.0011	.0015	.0013	.0009	.0007	.0006
Values for	.0021	.0026	.0024	.0018	.0009	.0010
Samples	.0027	.0034	.0035	.0028	.0010	.0006
1-3, KB						
Absorption	.0029	.0021	.0018	.0017	.0078	.0018
Values for	.0043	.0028	.0026	.0024	.0109	.0027
Samples	.0046	.0030	.0027	.0026	.0110	.0027
4-6, YL						

The data obtained from the KB/YL calibration runs were incorporated into a P-Matrix program supplied by Foxboro. This program provides the MIRAN 80 user an easy means of determining the concentration after proper calibration. The program is designed to take a measured absorbance and correlate it with a specific concentration. A complete explanation

of the program is provided in Appendix H. The source listing and menu-driven questions are contained in Appendix I. Table 32 is the output from the P-Matrix. The experimenter enters the signs (or Plums), P-Matrix, and decimal shift into the MIRAN 80. Once that is accomplished, the MIRAN automatically determines concentration.

NOTE: It is important to understand that the MIRAN 80 responds with an absorbance value when there is some other compound present that has the same functional group as the compound used to calibrate the unit. The user is responsible for confirming that it is the compound of interest causing the MIRAN to respond and not some other material.

Table 32. MIRAN 80 P-Matrix Input Table

ABSORPTION COEFFICIENT MATRIX

9.790-004	1.420-003
8.149-004	9.952-004
.000	.000
4.250-001	1.275+000
2.125+000	.000
.000	.000

TRUE P-MATRIX (UNSCALED)

3.157-005	4.785-005	.000	-6.228-002	4.242-001	.000
1.533-003	1.089-003	.000	1.324+000	2.452-001	.000

(1) P-MATRIX (FOR "80")

0.	0.	0.	408.	2780	0.
10.	7.	0.	8677.	1607.	0.

(2) DECIMAL SHIFT NUMBER = 3

(3) SIGNS FOLLOW:

8
0

NOTE: NUMBERS (1)-(3) ARE INFORMATION NEEDED BY THE MIRAN FOR AUTO CONCENTRATION DETERMINATION.

The trials used to determine the MIRAN's capability involved the use of three calibrating concentrations (0.52, 1.56, 2.60 ppm for KB and 0.425, 1.275, 2.215 ppm for YL) selected to represent the low, mid, and high concentration ranges. This was acceptable because of the experimental conditions, the very low signal to noise ratio of the MIRAN 80, and the length of time required for a single calibration. In a non-controlled environment (Plant Environment) at least six points should be used to calibrate the unit. As an example, we generated a 9-point curve in

a parts-per-million range as indicated above for KB (see Figures 79-81). The slope of the 9-point calibration curve (reported on Figure 80) is 1.4635. The slope obtained from the plot of the averaging of six trials is 1.2327. All data used to produce these plots (Figures 75 and 80) were collected at the primary wavelength of 8.543 μm.

5. BIGEYE BOMB SHIPPING CONTAINER (AN APPLICATION OF THE MIRAN)

5.1 Challenge of a Bigeye Bomb Shipping Container with the MIRAN 80.

The closed loop calibration system, described in Appendix H, was connected to a Bigeye Bomb container at one end by a needle valve. A needle valve at the other end was connected to a high purity 1A Matheson nitrogen gas cylinder fitted with a two-stage regulator. The container lid was secured, and the closed/sealed container was purged with air. The flow through the container was 10 L/min as delivered by a two-stage regulator with a pressure of 15 psig at the second stage. After 35 min, the container vapor environment was analyzed. Background absorption values were observed at the wavelengths specifically chosen for both the KB and TEP components. Those wavelengths chosen for QL and YL indicated no absorbance (see Table 33).

Table 33. Initial Check of Shipping Container (QL Free) on 17 April 1986

Time (s)	Measured Absorption Values			
	KB	TEP	YL	QL
0	0.000	0.000	0.000	0.000
60	1.834	1.707	-0.003	-0.070
120	0.986	0.802	-0.001	-0.005
240	0.786	0.532	-0.011	-0.003
480	0.101	0.100	-0.010	-0.000
960	0.857	0.007	0.000	0.000
1920	0.103	-0.006	0.000	0.060
2840	0.0147	0.002	0.001	-0.000

The MIRAN 80 was disconnected from the container and purged with high purity air to check the integrity of the air source. This test indicated no absorbance at any of the preselected wavelengths for KB and TEP. The MIRAN 80 was reconnected to the container for further analysis of the vapor environment. Again, the absorption values at the wavelengths assigned to KB and TEP indicated their presence. This led us to suspect that the glue used in the bomb foam mounts was the cause of the interference.

Background values for the container were read and stored in the MIRAN. The unit's gain and zero settings were fixed, and the test

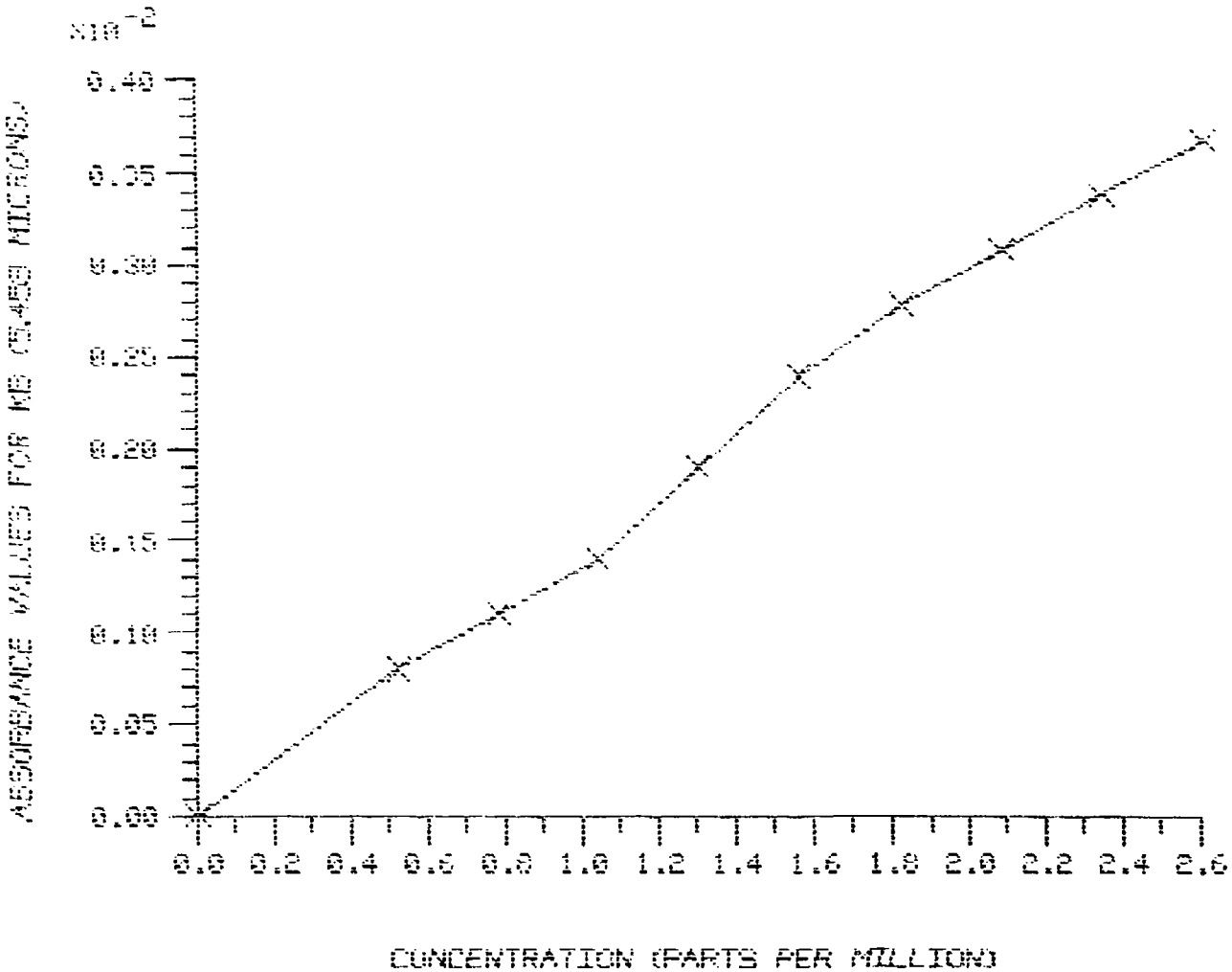


Figure 79. 9-Point Calibration Curve for KB

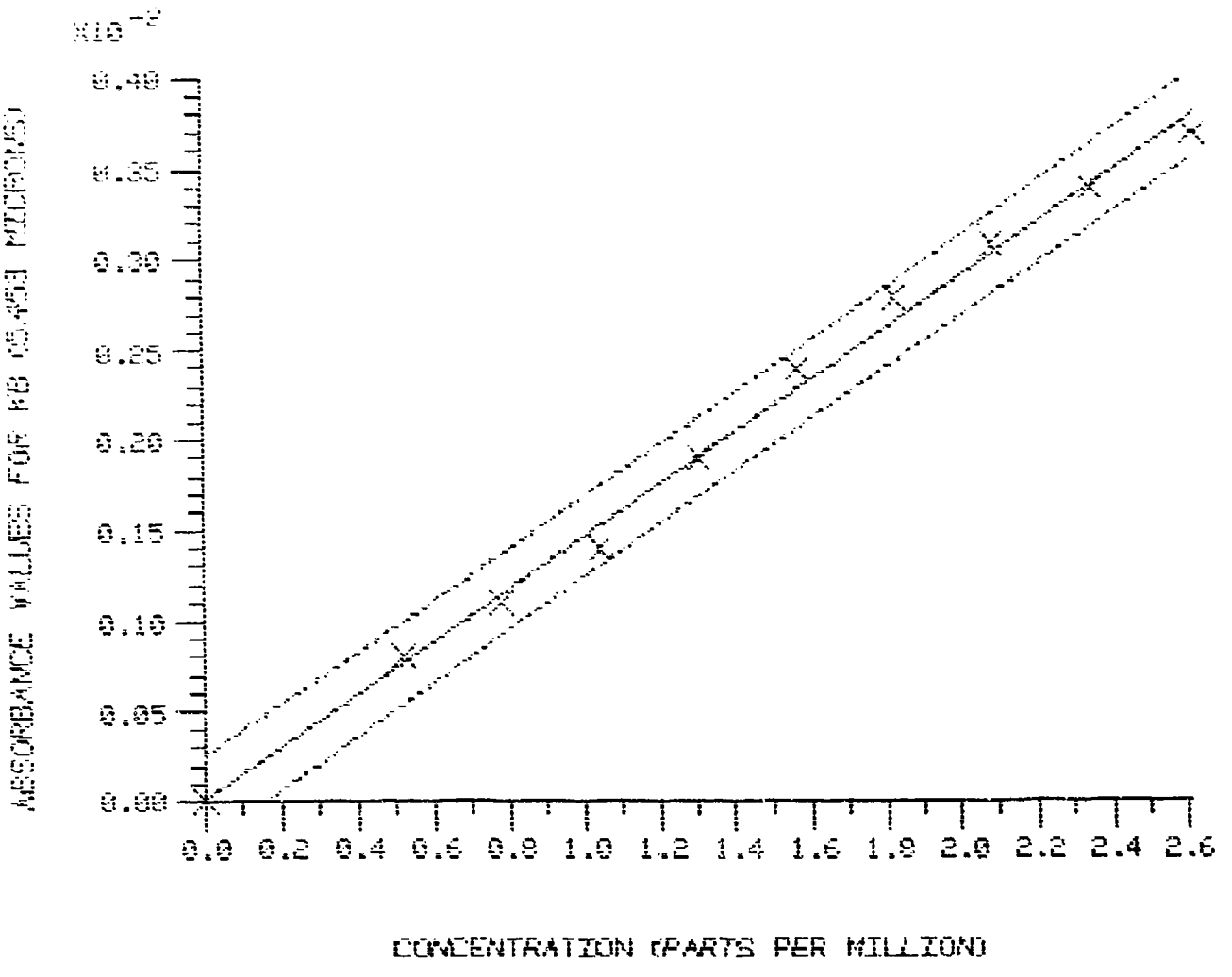


Figure 80. 9-Point Calibration Curve for KB with 95% Confidence Lines

```
DATA SET NO.  2                    MIRAN.KBGJ

X MEAN =        1.40400            X STD.DEV.=        .833083
Y MEAN =     2.060000-03           Y STD.DEV.=     1.222202-03

Y= 5.1940-06+1.4635-03X%
ANAL.OF VAR.          DF    SUM OF SQUARES     MEAN SQUARE       STD. ERROR
DUE TO REG.            1      1.337906-05       1.337906-05       3.657740-0
...3
ERROR ABOUT REG.       8      6.493506-08       8.116883-09       9.009374-0
...5
TOTAL                  9      1.344400-05
 F TEST:       1648.30
 COEF.OF DETERMINATION:    .995170
```

Figure 81. Statistical Values for Figure 80

begun. Data points were read over a 90-min interval. As shown by the data, little, if any, absorbance was at the wavelengths preselected for the YL and QL components.

The Bigeye Bomb shipping container was reopened to pour 4 mL of 90% QL over the bombs, and the container lid was replaced and sealed. The container with the same HP air flowing was continuously analyzed with the MIRAN. Over time, absorption values indicated the Presence of QL without its degradation or hydrolysis products. Periodic analyses of the effluents were obtained until the absorbance value stabilized for the component in question. No absorbance was indicated at the preselected wavelengths chosen for YL (Tables 34-39). Figures 82-85 are plots of the purge profiles of the container test. These data were extracted from Table 34.

Table 34. Container Challenge on 17 April 1986, Run 1

	Measured Absorption Values			
Time	KB	TEP	YL	QL
0	0.000	0.000	0.000	0.000
60	1.6389	1.5300	-0.0004	0.0013
120	0.1290	-0.0015	-0.0015	0.0030
240	0.1371	-0.0016	-0.0016	0.0032
480	0.1301	-0.0017	-0.0015	0.0027
960	0.881	-0.0005	-0.0008	0.0021
1920	0.0616	-0.0003	-0.0005	0.0010
2840	0.0150	0.0001	0.0004	0.0014

Table 35. Container Challenge on 17 April 1986, Run 2 (Instrument Rezeroed)

	Measured Absorption Values			
Time (min)	KB	TEP	YL	QL
0	0.0150	0.0001	0.0000	0.0002
1	0.0328	0.0001	0.0004	0.1114
2	0.0644	0.0000	0.0000	0.0018
3	0.0795	0.0000	0.0000	0.0024
4	0.0887	0.0000	0.0000	0.0025
7	0.1310	0.0000	0.0000	0.0020

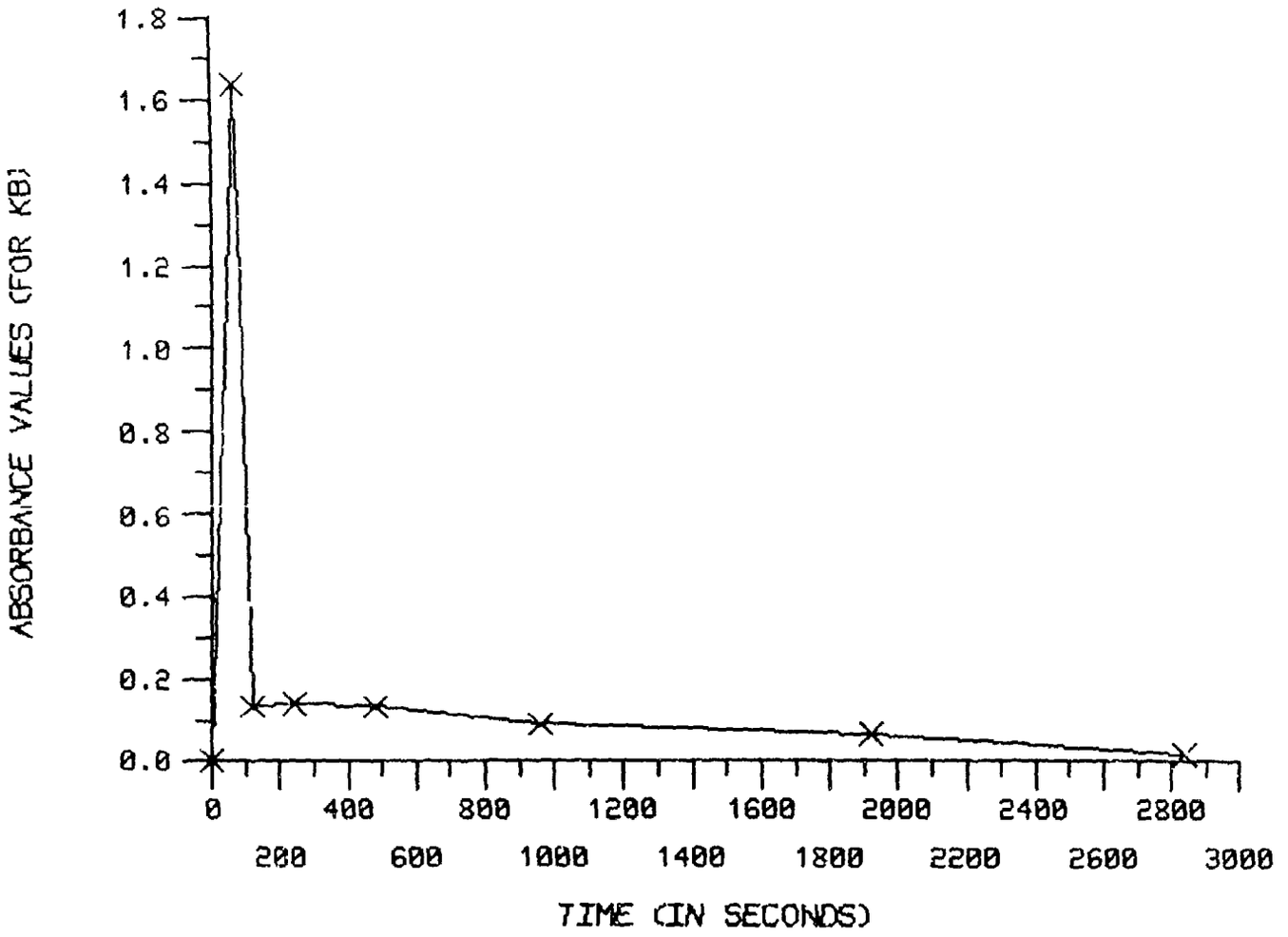


Figure 82. Purge Profile Over Time for KB

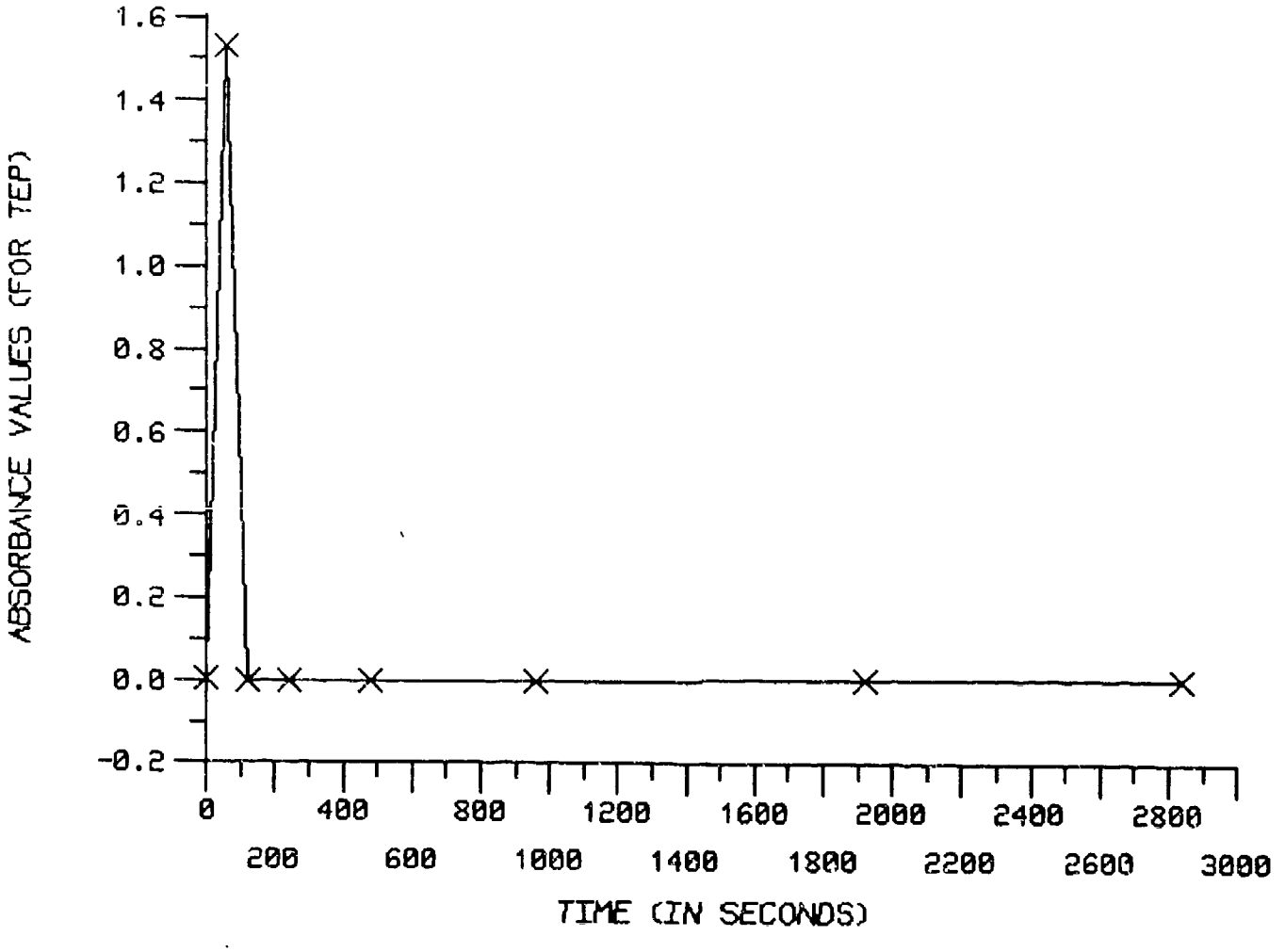


Figure 83. Purge Profile Over Time for TEP

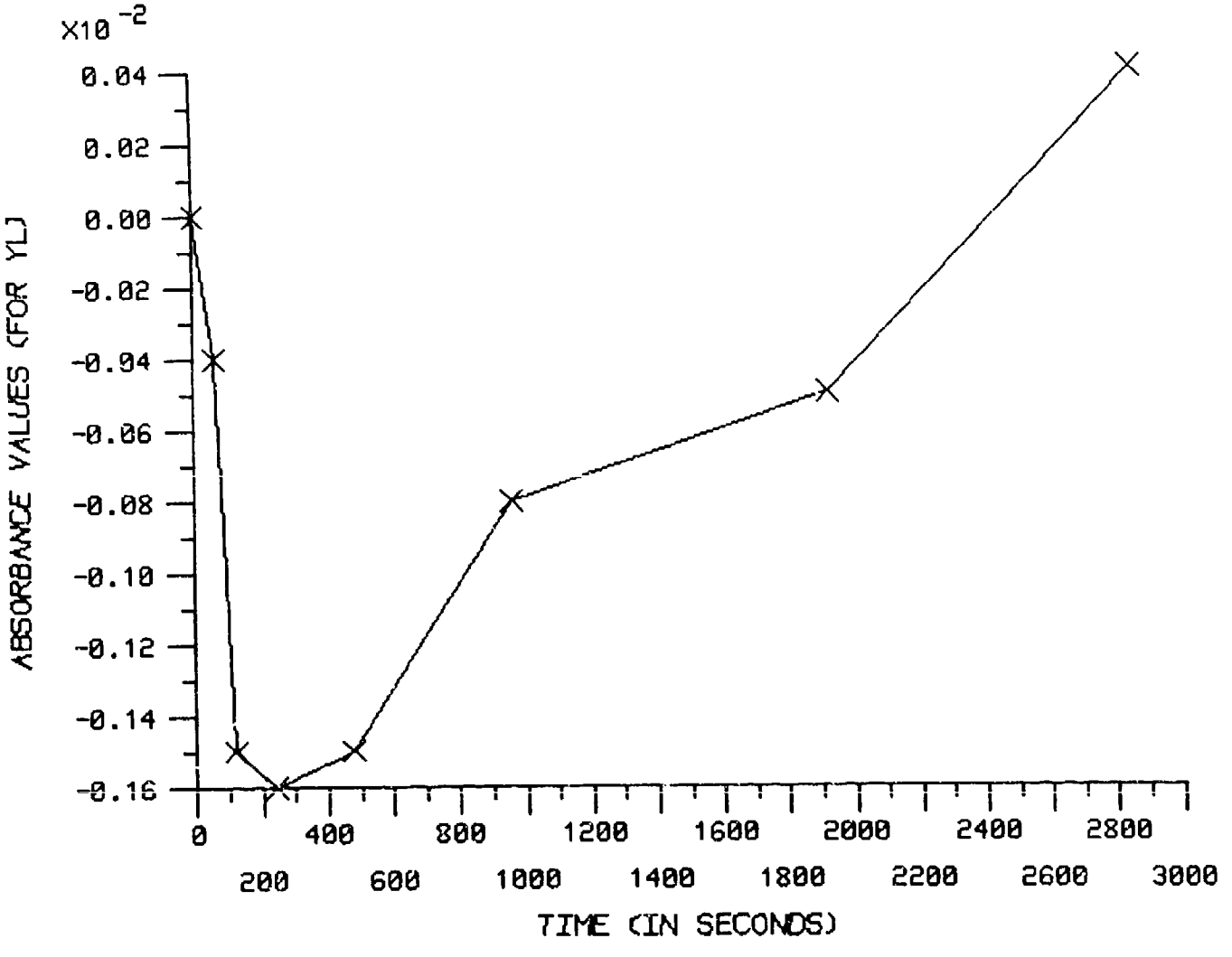


Figure 84. Purge Profile Over Time for YL

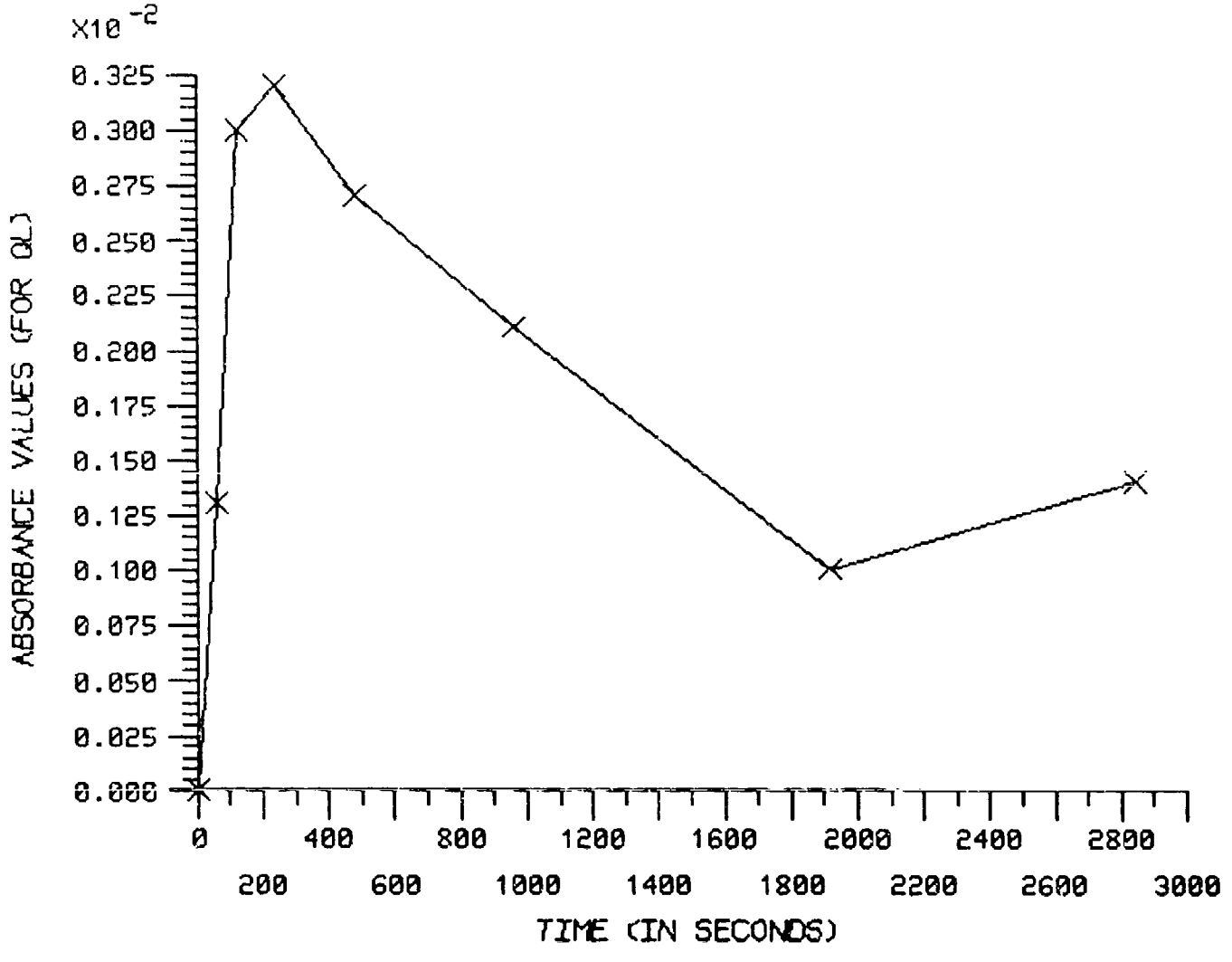


Figure 85. Purge Profile Over Time for QL

Table 36. Container Challenge on 17 April 1986, Run 3

Time (min)	Measured Absorption Values			
	KB	TEP	YL	QL
0	0.0624	0	0	0.0009
10	0.0916	0	0	0.0031
20	0.1586	0	0	0.0029
30	0.1655	0	0	0.0037

Table 37. Container Challenge on 18 April 1986, Run 1

Time (min)	Measured Absorption Values			
	KB	TEP	YL	QL
0	0.0000	0.0001	0.0000	0.0000
1	0.0351	0.0007	0.0006	0.0018
5	0.0797	0.0004	0.0001	1.2902
10	0.1045	0.0000	0.0000	0.9668
15	0.1209	0.0000	0.0000	0.0035

Table 38. Container Challenge on 18 April 1986, Run 2

Time (min)	Measured Absorption Values			
	KB	TEP	YL	QL
0	0.1230	0.0003	0	0.0037
5	0.1377	0.0000	0	0.0035
10	0.1536	0.0000	0	0.0040
15	0.1657	0.0000	0	0.0040
20	0.1446	0.0000	0	0.0042
25	0.1802	0.0000	0	0.0041
30	0.1855	0.0000	0	0.0044
35	0.1875	0.0000	0	0.0045
40	0.1873	0.0000	0	0.0047
45	0.1868	0.0000	0	0.0047
50	0.1859	0.0000	0	0.0050
55	0.1836	0.0000	0	0.0048
60	0.1823	0.0000	0	0.0050
65	0.1812	0.0000	0	0.0046
70	0.1798	0.0000	0	0.0044

Table 39. Container Challenge on 7 May 1986

Time (Min)	Measured Absorption Values			
	KB	TEP	YL	QL
2	0.0010	0.0009	0.0089	0.0010
4	0.0025	0.0022	0.0230	0.0029
6	0.0065	0.0047	0.0369	0.0044
8	0.0159	0.0099	0.0602	0.0072
10	0.0310	0.0125	0.0706	0.0093
12	0.0260	0.0150	0.0794	0.0108
14	0.0307	0.0177	0.0874	0.0126
16	0.0349	0.0197	0.0942	0.0140
18	0.0389	0.0217	0.1004	0.0153
20	0.0429	0.0238	0.1063	0.0171
22	0.0466	0.0257	0.1114	0.0188
24	0.0498	0.0274	0.1159	0.0192
26	0.0530	0.0290	0.1200	0.0210
28	0.0560	0.0305	0.1238	0.0217
30	0.0588	0.0321	0.1271	0.0230
32	0.0616	0.0333	0.1303	0.0242
34	0.0640	0.0347	0.1332	0.0249
36	0.0780	0.0418	0.1479	0.0305
38	0.0795	0.0426	0.1493	0.0307
40	0.0810	0.0434	0.1508	0.0320
42	0.0824	0.0442	0.1522	0.0322
44	0.0837	0.0447	0.1532	0.0330
46	0.0850	0.0455	0.1547	0.0335
48	0.0861	0.0460	0.1555	0.0336
50	0.0870	0.0463	0.1562	0.0339
52	0.0880	0.0468	0.1571	0.0344
54	0.0890	0.0474	0.1580	0.0352
56	0.0898	0.0477	0.1587	0.0353
58	0.0908	0.0484	0.1596	0.0359
60	0.0912	0.0487	0.1599	0.0363
62	0.0921	0.0489	0.1607	0.0359
64	0.0929	0.0495	0.1613	0.0368
66	0.0936	0.0499	0.1617	0.0366
68	0.0941	0.0502	0.1622	0.0370
70	0.0948	0.0502	0.1626	0.0367
72	0.0953	0.0507	0.1633	0.0381
74	0.0959	0.0510	0.1635	0.0384
76	0.0966	0.0515	0.1640	0.0378
78	0.0968	0.0516	0.1644	0.0385
80				
82				
84				
86				
88				
90				

After 24 hr, the container was reanalyzed. Results indicated that the QL vapor concentration had increased over the levels of the previous day. What was not expected was the absence of the hydrolysis breakdown components, KB and YL. From these results we can infer that the hydrolysis rate of QL in the vapor phase is slower than in the liquid phase (Tables 35 and 38). After 20 days, the container was reexamined using the same procedure. Because the container could not be purged, the MIRAN was zeroed (using the high purity air source) before connecting to the container. The container was monitored for an additional 90 min after which time several measured absorption values exceeded the maximum value of 1.00 au. The minimum reading was greater than the absorbance that corresponds to a 5 ppm concentration at the YL component's wavelength (Table 39). The same container challenge was repeated using a portable MIRAN 1B, which gave essentially the same results.

5.2 Results from Challenge of Container.

Challenge of the Bigeye Bomb shipping container was successful. Absorption values for a reference (4.645 μm), YL (10.599 μm), KB (2.848 μm), TEP (9.950 μm), and QL (13.755 μm) indicate that the MIRAN 80 is useful as a container monitoring system. The wavelengths were chosen from the FTIR spectra of the QL components.

Concentration values for the lowest obtained absorbance cannot be derived for QL because liquid calibration data have not been obtained for this compound.

For KB, minimum detectable limits cannot be provided due to possible glue absorption interferences over 2-3 μm.

6. PROBLEMS AND RECOMMENDATIONS

Our assessment of the MIRAN indicates that the unit can detect KB and YL in parts-per-million. The unit has reproducibly provided results in this calibrated and measured range.

The MIRAN 80 source element lasts approximately 3-4 months with continuous use. Replacement elements can be purchased from Foxboro Instrument Company, Foxboro, MA.

Two trained operators should be available to operate and maintain the units. An operator can prevent the collection of invalid data by routine checks.

There are several methods of calibrating the MIRAN units. The current studies used the liquid-injection, closed-loop method. Regardless of the calibration techniques, calibration in the range of interest is essential for an accurate assessment of airborne concentration. For KB and YL, the MIRAN 80 cannot be reliably calibrated in ranges lower than 0.4 ppm.

The MIRAN 80 units have the capability to circulate room air into and out of the cell. This capability was not used in the current studies because of the need to evaluate a continuous stream of KB and YL samples. A plant method for analyzing the room air (plant air) must be devised.

Gas samples of the QL components were not analyzed in a humid environment with the MIRAN. Whether the humidity will be a problem with the system has not been determined. An appreciable amount of time is required before a stable absorbance value is obtained once QL enters the cell. A plot of absorbance versus time is provided as an indication of the time required to lower QL concentration once in the cell. The following data (Figure 85) was obtained from the container test, see section 5.

Although not attempted in these studies, data collection with this unit can be automated.

Alarm level capability does exist with the system, and Foxboro has provided literature to assist in the development of alarm warning circuitry.

A method of continuously monitoring the environment must be developed.

The MIRAN 80 has an overheating proble, which was corrected in the newer MIRAN 980. This problem will have to be considered if the unit is used.

Other Systems or Technology.

Other more sophisticated systems, which are computer controlled, respond to a match of the component spectra in the environment with stored spectra. One such system uses an interferometer to assess the compound in the environment. Manufacturers of these systems are willing to provide customized turn-key systems. For information, contact:

Foxboro's Instrument Company, Foxboro, MA

Telos Laboratory, Fremont, CA

Hewlett-Packard Company, Boise, ID

Perkin-Elmer Corporation, Eden Prairie, MN

Proanco Incorporated, Fremont, CA

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APPENDIX A

OPERATION OF THE PA 260 ANALYZER

A. Equipment:

1. PA260 Detector with Set of Options

2. High purity hydrogen supplied from a cylinder or hydrogen generator.

3. Two stage hydrogen regulator CGA 380.

4. Recorder with input levels of 0-100 mullivolt or 0-1.0 volt.

5. Options:

Auto Ignition

Mode Switch
Auto Zero and Span Check Timer
Opt S-25 Charcoal Filter (Zero Air Column)

B. Operational Specifications:

Sample flow rate	Approximately 240 mL/min
Hydrogen flow rate	Approximately 125 mL/min
Power requirements	115 + 10 Vac (60 Hz) 250 Watts
Recorder outputs	Log output standard 0-100 millivolts or 0-1 volts
Relative humidity	0-99 %
Ambient temperature range	10-40 °C
Hydrogen (high purity)	3.1-4.2 Kg cm (45-60 psig)

C. Set Up Procedure:

Note: As a precaution, the power cord should be connected to the AC sources.

1. Pneumatic

a. Scrubber to zero air source column options:

Mount the zero air column (screw cap at the top) with the two hinged clamps attached to the rear panel. The top fitting is the outlet of this column and, in normal operations, is connected to the zero air port of the rear panel.

b. Sample lines:

Teflon tubing is recommended for all external lines. Also the source must be at "1 atmosphere" pressure when being introduced into the analyzer. Lines should be limited to approximately 6 foot lengths. Connect

a 1/8-in. od Teflon sampling line to the "Sample Direct" inlet. The other end of this line should be connected to a sample manifold or other outside ambient source. The connection of any other line depends upon which options are included with the analyzer.

c. Exhaust line:

When venting the analyzer exhaust gases to an area removed from the analyzer, a 1/4-in. od exhaust line may be connected to the port on the back panel marked "Exhaust."

d. Hydrogen line:

Hydrogen is a flammable gas. Use metal connecting tubing and check for leaks at all connections. Use a hydrogen cylinder regulator with a limiting orifice. If hydrogen cylinder is not in a vented area, the regulator safety relief valve should be vented to the outside. Connect a 1/8-in. od stainless steel hydrogen supply line to the port on the back Panel marked "hydrogen." If an external hydrogen shutoff valve is to be used, connect wires to the electrical plug.

2. Electrical:

a. Connect a recorder or other readout device to the appropriate output jacks on the back panel.

b. Put auto-reignite switch on the front panel in the "off" position.

c. With the power switch in "off" position, connect the power cable to 115 vac, 60 Hz, three-wire, grounded power source.

The analyzer is now set up to use zero air in the procedure below.

D. Start-up Procedure:

After completion of the set-up procedure, the detector is ready for start-up. (Before this procedure is performed, the detector should be sampling from a zero air source.) Proceed as follows:

1. Adjust the hydrogen supply inlet pressure at 45 psig. Check all hydrogen connections for possible leaks before proceeding.

2. Place "Range" switch in "log" position.

3. Place "Time Constant" switch in 10 s position.

4. Place "Mode" switch in zero position (if applicable).

5. Push the "Power" switch to the "on" position. The "power" and "ignition" switches should light, and the pump should start running.

6. Allow the burner block assembly to warm up for 20 min. The automatic temperature controller is factory set to warm up the assembly

and maintain the proper operating temperature level. The two temperature indicator lights on the front panel should be blinking.

7. Depress the "Ignition" button.

NOTE: The hydrogen flow should rise to the approximate setting listed on the calibration data sheet or "Hydrogen" flowmeter. If not correct, adjust the hydrogen flow to the correct setting. After several seconds, release the "ignition" button. If the ignition button is illuminated, the flame is not burning. After waiting until there is no flow indicated by the hydrogen flowmeter (approximately 30 sec), press the ignition button again for 10-20 sec. This latter step may need repeating several times to purge air from the hydrogen lines before the detector will light.

8. After ignition, set the hydrogen flow to the value listed on the calibration data sheet supplied with the detector or printed on the front Panel near the bottom of the flowmeter.

9. Allow 15 min for the internal temperature of the instrument to stabilize and re-set the hydrogen as before.

10. Place the range and time constant switches in the desired positions.

11. Place the detector in sampling mode by using the procedure that relates to your particular unit.

12. Allow 15 min for the internal temperature to stabilize. Remove the zero air source line from the port marked "Sample Indirect." Remove the cap from the "Direct Inlet" port and place it on the "Sample Indirect" Port. Connect sample line to the "Direct Inlet" port.

Note: If sample air is introduced through the "Sample Indirect" port for extended periods of time, the "Air" flowmeter can become dirty and contaminated with gases and will affect the detector response time.

The analyzer is now ready for calibration. If the analyzer was calibrated recently and the flame was out for a short time, recalibration is not necessary if a zero and span check indicate no change in span.

E. Analyzer Calibration Procedure:

The following calibration steps should be performed on each range to be used. The time constant (usually 1.0) for each range (1x10-8 to $1x10^{-5}$) should be set in the position most often used for that range.

1. Introduce (at ambient pressure) zero air into the sample line.

2. Set the "Range" switch to the lowest range.

3. After a stable reading is obtained adjust the "zero" control on the front panel so that the analyzer output reads 0.0 volts on a digital volt meter or a chart recorder.

APPENDIX A

4. Set "Range" switch for the highest ranges ($1x10^{-8}$) to be calibrated.

5. Introduce (at ambient pressure) a phosphorus concentrate equivalent to 90% full scale of the range to be calibrated.

6. For each range to be calibrated, introduce accurately known concentrations approximately equivalent to 75, 60, 30, and 15% of full scale concentration for that range and zero air. Convert the voltage (or percent charge reading) to current, and record the current reading for each concentration.

7. Put the current output (or percent chart) versu. concentration for each range on log-log paper. These curves represent the calibrated output of the analyzer for each range.

APPENDIX B

GAS CHROMATOGRAPHIC PARAMETERS FOR THE ANALYSIS OF QL AND RELATED PRODUCTS

Column Type	Fused-silica capillary with Durabonded - 5 stationary phase
Column Dimensions	15 m long 0.5 mm od 0.25 mm id
Temperature Program	Isothermal at 80 °C for 3 min Programmed at 7 °C per min to 250 °C.
Carrier Type and Flow Rate	Nitrogen at 1 cm^3/min
Injection Mode	Split mode @ 600:1
Sample Size	microliters

Blank

APPENDIX C

NUCLEAR MAGNETIC RESONANCE (NMR) ANALYSIS OF OMNIBUS SAMPLES

A. General

Each neat sample was placed into a clean, dry 5-mm od. Pyrex NMR tube. The tube was capped with a pressure cap, and the top of the tube was wrapped with Parafilm. Multinuclear NMR spectra were run of each sample as noted below:

1. Diethyl Methylphosphonite (TR) - H and P.
2. Triethyl Phosphate (TEPA) - H and P.
3. Triethyl Phosphite (TEP 1) - H and P.
4. Ethyl MethylPhosphonite (YL) - C and P.
5. Diisopropylaminoethanol (KB) - H and C.
6. Diisopropylaminoethyl Ethyl Methylphosphonite (QL) - H and P.
7. Bis-Diisopropylaminoethyl Methylphosphonite (LT) - C and P.

For each sample and for each nucleus, the entire chemical shift range for that nucleus was scanned at high amplitude so that all impurities would be detected. The overall mole % purity for each sample was calculated using the information from all spectra records for that sample, where possible identification of the impurities present was made so that a weight percent purity for the sample could be calculated.

B. Instrumental

The H NMR spectra were recorded using a Varian EM-390 NMR Spectrometer operating at 90 MHz. Spectra were recorded at probe temperature (~34 °C) and quantitative data were obtained by electronic integration.

The C and P NMR spectra were recorded using a Varian XL-200 Superconducting Multinuclear NMR System operating at 50 MHz for C observation and 81 MHz for P observation.

C Spectra: Spectra were obtained at probe temperature (~22 °C, XL-200), and tetramethylsilane (TMS)/chloroform (CHCL) was used as the external reference. For each sample analyzed, at least 200 transients were accumulated using a pulse width of ~35, a sweep width of at least 240 ppm, an acquisition time of at least 1 s, and a pulse delay of at least 2.5 s. Full proton noise decoupling was used, and "quantitative" data were obtained by digital integration of the peak areas.

P Spectra: Spectra were obtained at probe temperature (22 °C, XL-200) and phosphoric acid (85%) was used as the external reference. For each sample analyzed, we used at least 246 ppm, an acquisition time of at least 1 s and a pulse delay of at least 2.5 s. In addition, gated proton noise decoupling was used to eliminate any effects from nuclear Overhauser enhancement (NOE). Quantitative data were obtained by digital integration of the peak areas.

APPENDIX C

APPENDIX D

FILLING, CALIBRATION, AND USE OF DIFFUSION AND PERMEATION TUBES AND STANDARD GENERATORS/CALIBRATORS

1. Concept

a. Several small devices are used to release dilute concentrations of various materials into an air (gas) flow system. These devices are called generators and are used to release material continuously and dynamically at a predetermined low level vapor concentration diluted by a flow air (gas) stream. The generators include (require) permeation and/or diffusion tubes for a known source and require accurate temperatures and gas flows that must remain constant to obtain a known, reproducible and accurate dilute vapor concentration. The generators are provided with a variable temperature controller, which ranges from 25 to 80 °C. A meter (digital readout) provides confirmation of the selected temperature, which has a control band of +0.1 °C.

b. Compressed air (gas) supplied either to the front or rear of the instrument is used as the diluent. This air is cleaned by a filter. The pressure is regulated by an internal panel adjustable pressure regulator. Two flow meters or other gas measuring devices provide for the measurement and control of both the chamber airflow and diluent airflow. Both the flows are adjustable from the front panel.

2. Step-by-Step Procedure

a. Set up

(1) Read and understand the operation and service manual for the calibration system.

(2) Place the calibration system in an approved agent hood.

(3) Place syringe with needle in working hood (agent approved).

(4) Place decontamination solution as required in SOP 8-1-83 1, Annex D, in working hood.

(5) Set timer for length of time that is permitted for the type of gases being used.

(6) Start the calibration system, and allow the chamber temperature to reach the desired temperature and to stabilize.

b. Filling and Calibration - Permeation Tube

(1) Seal one end of permeation tube, and place it in a 10-mL beaker.

(2) Fill syringe or pipette with compound (about 1 mL).

(3) Insert tip of syringe needle or pipette into permeation tube to the depth of 10% from the top.

(4) Dispense compound into permeation tube (NOTE: be sure to leave at least 10% liquid void).

(5) Remove syringe or pipette from permeation tube,

(6) Force Teflon or appropriate plug into permation tube.

(7) Put wire binding on permeation tube to hold plug in Place.

(8) By use of tweezers or tongs, place permeation tube into the generator's chamber. Seal chamber and start generator at desired airflow and temperature. Flow rates and temperature are selected based on manufacturer's specifications (NOTE: Allow at least 24 hrs for the permeation tube to come to equilibrium).

(9) By use of tweezers or tongs, remove permeation tube from generator's chamber. (NOTE: Be sure NOT to contaminate the permeation tube with finger prints, dirt, etc). Place the permeation tube in a tared 10-mL beaker that has been weighed to the nearest 0.1 mg.

(10) Weigh the permeation tube and 10-mL beaker on an analytical balance, and record weight to nearest 0.1 mg.

(11) Replace the permeation tube into generator's chamber, seal chamber, and start generator. (NOTE: Record the airflow, time, temperature, and pressure).

(12) Measure the vapor or output by bubblers or other measuring devices.

(13) Repeat steps 9-12 until ratio of weight loss/time is constant (R).

c. Filling and Calibration - Diffusion Tubes

(1) Place diffusion tube in glass carrier.

(2) Fill syringe having a 6-in. needle with compound.

(3) Place needle into diffusion tube.

(4) Dispense compound into diffusion tube - (maximum 5 mL).

(5) Remove syringe from diffusion tube.

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(6) By use of tweezers or tongs, place the diffusion tube into the generator's chamber, seal the chamber, and start generator at desired airflow and temperature. (NOTE: Allow at least 24 hr for the diffusion tube to come to equilibrium).

(7) By use of tweezers or tongs, remove the diffusion tube from generator's chamber. (NOTE: Be sure NOT to contaminate the diffusion tube with finger prints, dirt, etc). Place the diffusion tube in a tared glass carrier that has been weighed to the nearest 0.1 mg.

(8) Weigh the diffusion tube and 10-mL beaker on an analytical balance until ratio of weight loss to time is constant.

(9) Replace the diffusion tube into generator's chamber, seal chamber, and start generator. (NOTE: Record the flow, time, temperature, and pressure).

(10) Measure the vapor output by bubblers or other measuring devices, and analyze the output concentration.

d. Operation.

(1) Operator will read and understand instruction manual for instrument.

(2) Install precalibrated diffusion/permeation tube into preheated oven and close oven. (NOTE: Diffusion tube must remain upright during storage and transfer).

(3) Calculate dilute effluent concentration according to calibration value of tube and the instruction manuals.

e. Permeation Tube.

(1) By use of tweezers or tongs, remove tubes from generator.

(2) Place permeation tubes in clamp so the permeation tube is vertical.

(3) Using single blade razor or sharp knife, cut and open tube well above the liquid level.

(4) Clean permeation tube and razor blade or sharp knife with a solvent washing then discard permeation tube.

f. Diffusion tubes.

(1) By use of tweezers or tongs, take glass diffusion tubes from generator.

(2) Place diffusion tubes in a clamp in a beaker so that the tube is vertical.

(3) Using a syringe and a long needle, remove diffusion tube and extract the excess compounds from the diffusion tube.

(4) Clean diffusion tube and needle by solvent washing. Fill and empty the tubes four times using a syringe and fresh isopropyl alcohol for each wash.

APPENDIX E

VAPOR GENERATOR (SPANLAB MODEL 580-3C)

1. INTRODUCTION

The SpanLaB 580-3C is a three-channel, precision gas standards generating system. It is designed to provide a continuous flow of precise, low concentration, variable composition, multicomponent gas mixture.

Interchangeable trace source permeation modules are used to control the mixture concentrations. Each trace source module dispenses a very small flow of a component gas into a much larger carrier gas flow to form the calibration mixture.

The 580-3C provides three independently controlled permeation units. The multicomponent mixture (SUM) can contain any combination of the component outputs from these units. The composition of this mixture can be instantaneously changed from the front panel of the instrument. Alternately, the output of each permeation unit can be used separately to provide three simultaneous, independent, binary mixtures. The system Provides precise controls for permeation oven temperatures, dilution flows, and component gas pressures. Dilution flows are measured by an electronic mass flowmeter and displayed digitally.

Trace concentration mixtures are made directly from pure compounds in a precise single step dilution. By varying operation parameters, the mixture concentration can be adjusted over a wide range.

Versatility is the key feature of the Model 580-3C. It adapts to use any standard type of permeation or diffusion source, so it offers the widest possible choice of mixture components and concentration ranges. It can prepare mixtures of most gases and vapors at concentrations ranging from sub-parts-per-billion to over 1,000 ppm. Using the unique Trace Source Series 57 gas fed modules, even mixtures containing high pressure component gases like CO, COS, NO, CH_4, HCl, O_2 , N_2, and H_2 can be made. The background gas can be almost any corrosive gas.

A complete range of accessories and special features makes this instrument adaptable for use with any high sensitivity gas analyzer.

The 580-3C is an invaluable tool for any work requiring multi-component, low concentration, variable composition gas mixtures. The capability of rapidly changing the mixture composition on-line is of special interest for dynamic studies. Some typical applications of the 580-3C are:

Rapid, Multi-Point Calibration of Multi-Component Analyzers.

Simultaneous Single "Component" Calibration of Several Analyzers.

Testing Interference and Cross Sensitivity Effects in Analytical Method Development.

Odor Research - Permits Evaluation of Synergistic Effects from Combinations of Odorants.

Simulating Contaminated Environments for Health Effects or Equipment Life Studies.

Studies of Long Term Synergistic Health Effects of Toxicants at Sub-TLV Levels.

Catalysis Research and Development - Used for rapid evaluation of the effect of trace, vapor phase components as catalyst poisons or stabilizers, reaction rate inhibitors or accelerators, and source of by-products formation.

Generating Data for Mathematical Modeling of Real Vapor Phase Reaction Systems (tremendously speeds multi-level, multi-variable, repetitive point experimentation required for using regression techniques to create models reflecting the effects of reactant purity).

2. PRINCIPLE OF OPERATION

The 580-3C is basically a three-channel gas dilution instrument. It uses molecular permeation of vapors through a polymeric membrane as the controlling mechanism to establish a very small, stable, and reproducible flow of component compound vapor which is mixed with a much larger flow of dilution gas. This mixture is then delivered immediately to the analyzer, thus minimizing the effect of changes in mixture concentration due to reaction and adsorption of trace components in the mixture.

The concentration of each component in the gas mixture is given by:

$$C = \frac{f}{F+f} \quad 10^6 \qquad (1)$$

where:

C is the concentration in parts-per-million, f is the flow of the component gas, and F is the flow of a dilution gas through the permeation device.

In practice the dilution flow, F, is very much greater than the component permeat, f. Thus the concentration equation reduces to

$$C = \frac{f}{F} \quad 10^6 \qquad (2)$$

The diluent flow, F, is established by controlling a flow of a suitable gas from an external source. Typical gases used for this purpose are nitrogen air, carbon dioxide, argon, helium, etc.

In operation, a suitable trace source permeation module is installed in the instrument and allowed to equilibrate at specified operating conditions. In the trace source module, a supply of the pure component compound contacts one side of a rugged Teflon tube that serves as the permeation membrane and permeats through the tube wall.

Permeation through the membrane can be considered a classical diffusion through a solid. The flow of component gas through the membrane is given by:

$$f = \frac{KAP}{d} \qquad (3)$$

where

f = volume of gas in cubic centimeters at standard temperature and pressure (STP) flowing through the membrane each second.

K = the permeability of the membrane for that gas in

$$\frac{(cm^3 \text{ at STP})\ (cm)}{(s)\ (cm^2)\ (cm\ Hg)}$$

A = the membrane area in cm^2

d = the membrane thickness in cm.

P = the partial pressure differential of the permeating gas across the membrane in cm Hg.

The permeability function, K, is peculiar to each gas-membrane combination, and varies with temperature as:

$$K = K_o \exp(-B/T) \qquad (4)$$

where

Ko and B are constants determined by the gas-membrane combination, and T is the absolute temperature of the membrane in degrees Kelvin.

The mixture concentration can be adjusted by changing either the dilution flow rate or the permeation rate. In a trace source module, flow of component through the membrane is determined, as shown in equation 4 by its inherent physical characteristics, its operating temperature, and the partial pressure differential of component gas across it. Each trace source module has been pretested and is supplied with data describing its permeation rate as a function of these variables. In the 580-3C, each permeation unit provides precision controls that allow full adjustment of each of these parameters to give maximum concentration range ability.

Using this method, dilution of the pure component compound is accomplished in one precise step. The cumulative errors encountered in successive dilution methods are eliminated.

3. INSTRUMENT DESCRIPTION

3.1 General Description.

The SpanLab 580-3C contains three, independently controlled, Permeation units interconnected by inert (Teflon) solenoid valves. Physically, the system is mounted in two interconnected drawers, housed in a 24-in. wide instrument cabinet. The lower drawer contains the permeation units and all operating controls. The upper drawer houses an electronic, mass flow measuring unit for dilution flow measurement. The meter unit is manually multiplexed to provide measurement of all flows with a single meter unit.

The figure shows a flow diagram of the system. The dilution gas source enters through the rear of the instrument and is pressure regulated to approximately 20 psig. This regulated pressure is applied to a gas distribution manifold, which feeds four output pressures to the flow measure drawer. One output is provided for multicomponent (sum) dilution flow and each permeation unit has an output. In the flow drawer, each dilution source is routed either directly back to its respective permeation unit or through the mass flowmeter head and then back to its permeation unit. In the permeation drawer, each dilution flow regulator adjusts and maintains a steady flow of 0.25-2.5 L/min. The other portion of the flow passes through a three-way solenoid valve and feeds the oven-flow regulator. The oven-flow regulator adjusts and maintains a steady flow of 0.02-0.2 L/min over the permeation source. This flow passes through a preheated tube in the oven and joins with the permeate flow of component to form a primary mixture, which is routed through a pair of Teflon solenoid valves and either joins the main dilution flow for that unit, the sum flow, or is discarded to vent. When the oven flow and permeate are routed to the sum flow, the oven flow is taken from the sum flow, so measured flow for either mixture is always the actual total flow.

To provide the capability of filling series 57 gas-fed sources with component gas, each unit has an all stainless flow path with precision Pressure regulator and gauge, a preheat tube in the oven, a needle valve, and shutoff valve for flow control. For operational convenience, the component gases enter and exit, and each mixture exits through the front panel of the permeation drawer.

The preparation of precise low concentration gas blends using the permeation method requires accurate control of the permeation source temperature, precise control, and accurate measurement of the dilution flow rate and component gas pressure, and careful selection of materials in contact with the low concentration blend. The SpanLab 580-3C is designed to provide the high standards of precision and accuracy required in a Precision laboratory gas standards generator.

Each permeation unit has a high thermal mass heating system. Temperature is controlled at three pre-selected points by a precision, mercury-in-glass thermostat, coupled to the heating system by a zero-switching, solid state power switch. This simple system is a key feature of the instrument. Temperature settings have fixed, known accuracy, traceable to the NBS, and do not drift.

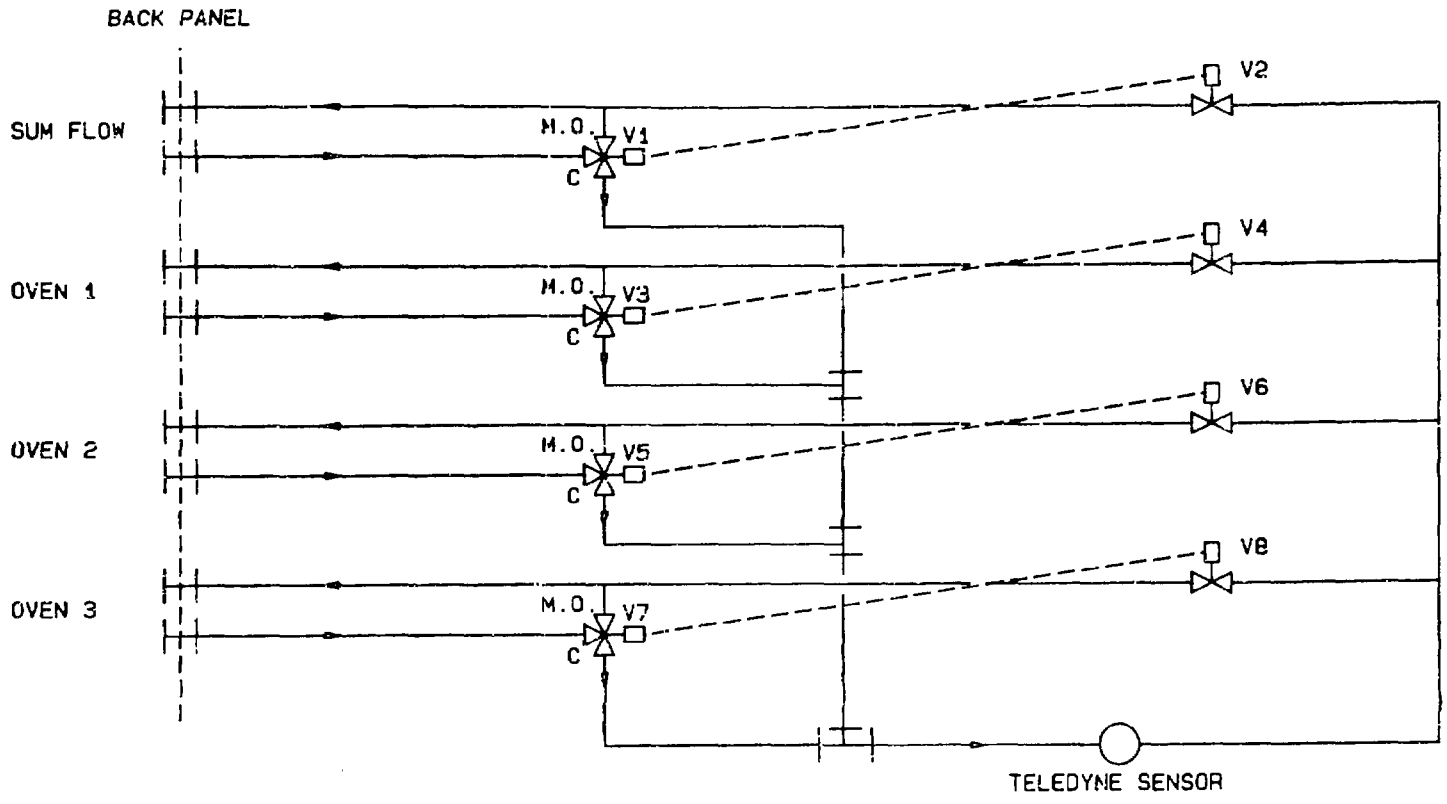

Figure. Flow Diagram of SpanLab Model 580-3C Mass Flow Unit

In the 580-3C, diluent gas flow rates are controlled by high quality, constant-differential-pressure type flow controllers. Flows are measured by a precision, electronic, mass flowmeter, with digital readout.

When gas fed trace source permeation sources (Type 57S or 57H) are used, the pressure of each "Component" compound fed to instrument is controlled by a precision, stainless steel non-bleed pressure regulator. A precision pressure gauge is provided to monitor feed pressure to each trace source device.

The low concentration blends contact only gas and Teflon (FEP and/or TFE) in the 580-3C. These materials are satisfactory for delivery adsorption and absorption of the component compound.

3.2 Permeation Unit Controls.

3.2.1 Front Panel Controls.

Gas Connections

Sum Output - Point where multicomponent mixture exits the system. Can contain any combination of components installed in the permeation units or may be dilution gas only. Connection is 1/8-in. n.p.t. female. Material is FEP Teflon. Recommend inert fittings and tubing.

Unit 1-3 Output - Point where individual permeation unit exits the system. Each output can contain the component installed in its respective permeation unit or may be dilution gas only. Connection is 1/8-in. n.p.t female. Material is FEP Teflon. Total of three connections; recommend inert fittings and tubing.

Unit 1-3 Component Gas In - Entry points for gaseous component compounds. Required when series 57 gas fed permeation sources are used; unused with disposable tubes, ULED, and LFH sources. Connection is 1/8-in. n.p.t. female. Material is 316 stainless steel. Recommmended Swagelok DESO type Quick Connect fitting for maximum convenience and safety. Alternate is any high quality resealable, 316 tube connector. Interconnecting tubing should be 316 stainless steel seamless or appropriately rated armored flex tubing. Component gas is usually pressurized. Total of three points.

Unit 1-3 Component Gas Out - Exit points for purge flow of gaseous component compounds. Connection is 1/8-in. n.p.t. female. Material is 317 stainless steel Recommend Swagelok DESO type Quick Connect fittings for maximum convenience and safety. Alternate is any high quality, resealable, 316 tube connector. This is a waste (vent) stream of possibly hazardous gas. Normally, expect stream to be at atmospheric pressure. Total of three points.

Dilution Flow Adjust

Needle valve adjustments are incorporated in each dilution gas flow controller. These valves are an integral part of the flow controllers. There are a total of four valves.

Component Gas Pressure Gauges

These are 4-in. pressure indicators for use in adjusting the component gas pressure in each series 57 permeation source. Standard range supplied is 0-60 psig. Standard bourdon tube material is 316 stainless steel. Normal accuracy of new gauges is +05% of full scale. These gauges indicate the total pressure of gas surrounding the permeation membrane in a series 57 source. There are a total of three gauges.

Component Pressure Adjust

Pressure regulator adjustment knobs for setting the pressure of component gas in the permeation source.

Units 1-3 Component Gas Flow Adjust

Needle valves used for limiting flow of the raw gases when the permeation chamber is being charged (or purged) with fresh component gas.

Units 1-3 Component Gas Shut Off

V-stem shut off valves used to block component gas flows during static operation.

Units 1-3 Function Switches

These switches route the primary mixture of component permeate in an oven flow either to the multicomponent (sum) output, the output of the unit itself, or to the discard gas vent. Indicator lights are provided to show if the mixture is routed to the sum or unit output.

3.2.2 Rear Panel Controls.

Gas Connections

Diluent In - Input for dilution gas to the system. Connection is 1/8-in. Swagelok (1/4-in. used for higher flow models). Material is brass.

Discard Vent - Exit point for unused primary mixture of components and oven flow. Connection is 1/8-in. n.p.t. female. Material is 316 stainless steel.

Flow Measure Outputs - Exit port for dilution flows to the flow measure drawer. Connections are 1/8-in. Swagelok brass tube. Total of four ports.

Flow Measure Returns - Input port for measured dilution flows from the flow measure drawer. Connections are 1/8-in. Swagelok brass tube. Total of four ports.

Oven Flow Adjust

Needle valve adjustments for each oven dilution flow controller.

The valves are an integral part of the low range flow controllers used to regulate the dilution flow contacting the permeation source. Total of three valves.

3.2.3. Internal Controls.

Electrical Controls

Each oven unit has its own electrical control assembly for turning the unit on and off, selecting the operating temperature, and selecting the input heat range. Controls on each panel are as follows:

Power Switch - Red push button switch. Push to turn power on to oven unit, push again to turn power off.

Power On Indicator - Red L.E.D. lamp. This light should glow continuously when power is on.

Heater Range Switch - Selects high (100 watt) or low (25 watt) heat input to the oven to provide balance of heat input to heat load. Press black button to select high (100 watt) input.

Heater Range Indicator - Red L.E.D. lamp. This light should glow continuously when the heater range switch is in the "high" Position.

Temperature Selector Switches - Each oven has three preset temperature set points. Pressing on the white, interlocking buttons selects that operating temperature.

Heater Indicator Light - Red L.E.D. lamp. This light glows when Power to the heaters is "on." Operation is on or off; there is no dim glow.

Oven Units

The permeation oven units are large insulated aluminum blocks located near the center of the drawer. Two 50-watt rod heaters are used to heat the block. Each block has three interchangeable, mercury glass thermo-switches, which provide the preset control temperatures. Heat transfer tubes for dilution gas and component gas preheat are installed in the assembly.

Temperature Controllers

The temperature controllers are the circuit cards mounted on the oven units.

The Model 580-3C uses an on-off control action. The temperature controller is based on an integrated circuit zero crossing detector and switch. The control circuit is designed so that when the oven temperature is below the set point (i.e., the thermoswitch is open) the control circuit is biased "on" to pass full power to the heaters. When the temperature reaches the set point and the thermoswitch closes, power is turned off as the voltage crosses zero during the next half - AC cycle. When the temperature drops

below the set-point and the thermoswitch again opens, power to the heaters is turned on as the voltage crosses zero during the next half AC cycle and each subsequent half cycle until the set point is reached and the thermoswitch closes again.

The temperature differential between opening and closing of the thermoswitches is approximately 0.05 °C.

3.3 Mass Flow Unit Controls.

3.3.1 Front Panel Controls.

Function Selector Switch

A five-position rotary switch is used to select stream flowing through the mass flow unit sensor.

Flow Meter Readout

A 3-1/2 place digital meter that indicates the mass flow of the various gas streams in the 580-3C.

3.3.2 Rear Panel Controls.

Gas Connections

Flow Input - Connections for input of flows from the permeation unit for flow measurement. Connections are 1/8-in. Swagelok tube fittings. Material is brass.

Flow Outputs - Connections for return of measured flows to the permeation unit. Connections are 1/8-in. Swagelok tube fittings. Material is brass.

APPENDIX F

ANALYSIS OF KB AND YL USING THE MIRAN 980

PROBLEM:

The PA 260 is capable of monitoring concentration levels of QL and hydrolysis products with the exception of KB. To monitor KB, the MIRAN 980 can be used. The levels of monitoring are less than 3 ppm.

MONITORING APPROACH:

The closed loop calibration technique described in the MIRAN 80 section was constructed, replacing the MIRAN 80 with the MIRAN 980. After construction of the system, 0 air (or the background air) was used to purge the 20 m cell. Throughout the analysis the 20 m cell path was selected.

Gas chromatography-Fourier transform Infrared spectra obtained from the U.S. Army Environmental Hygiene Agency (AEHA) were used to identify the specific analytical wavelengths for KB and YL. Due to possible interference by water vapor and carbon dioxide, wavelengths above 81 μm were chosen. Figures 1 and 2 contain the spectra of the two components. The following discussion explains how the wavelengths for KB and YL were chosen from the spectra. The values are precise for the MIRAN 80 and 980 used in our assessment. Our reference value was either 3.9 or 4.00 μm. Instrument slit width of 1 mm was used for all data collected.

The zero intercept analysis was decided upon because of the low need to measure concentrations. The absorbance versus. concentration (A/C) curves for each component are likely to be quite linear; therefore, it is logical that zero absorption will correspond to zero concentration. If the plot of absorbance versus concentration is non-linear, recalibration is required using the non-zero intercept mode of calibration.

The following parameters have been established:

1. Gas cell pathlength set at 20-25 m.
2. Slit width set at 1 mm.
3. MIRAN 980 has been given 10 min to equilibrate.
4. Recorder X-Y is connected to MIRAN, equilibrated and the base line set.

Step remaining before a calibration run can be performed is to determine the strongest absorption peaks observed by the MIRAN 980. This information was obtained by using the peak picked and digital scan features of the unit.

Obtain Specific Wavelength Values for MIRAN 980

First, a background spectrum of clean background air is measured and stored. A sample of KB vapor is introduced (via the closed loop liquid injection method or gas generator) and PEAK PICKER mode is used to locate the strongest

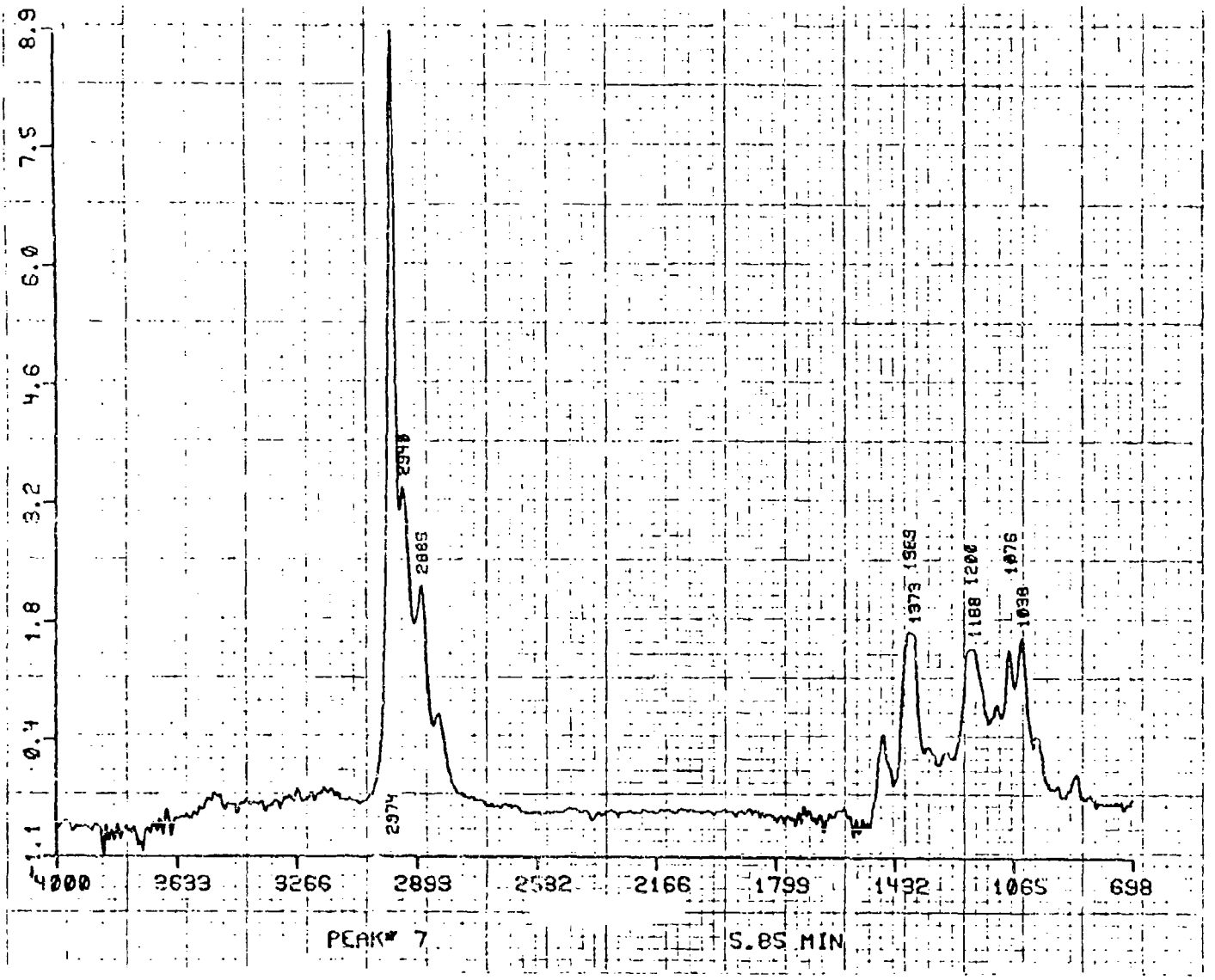

Figure F-1. Peak No. 7, KB

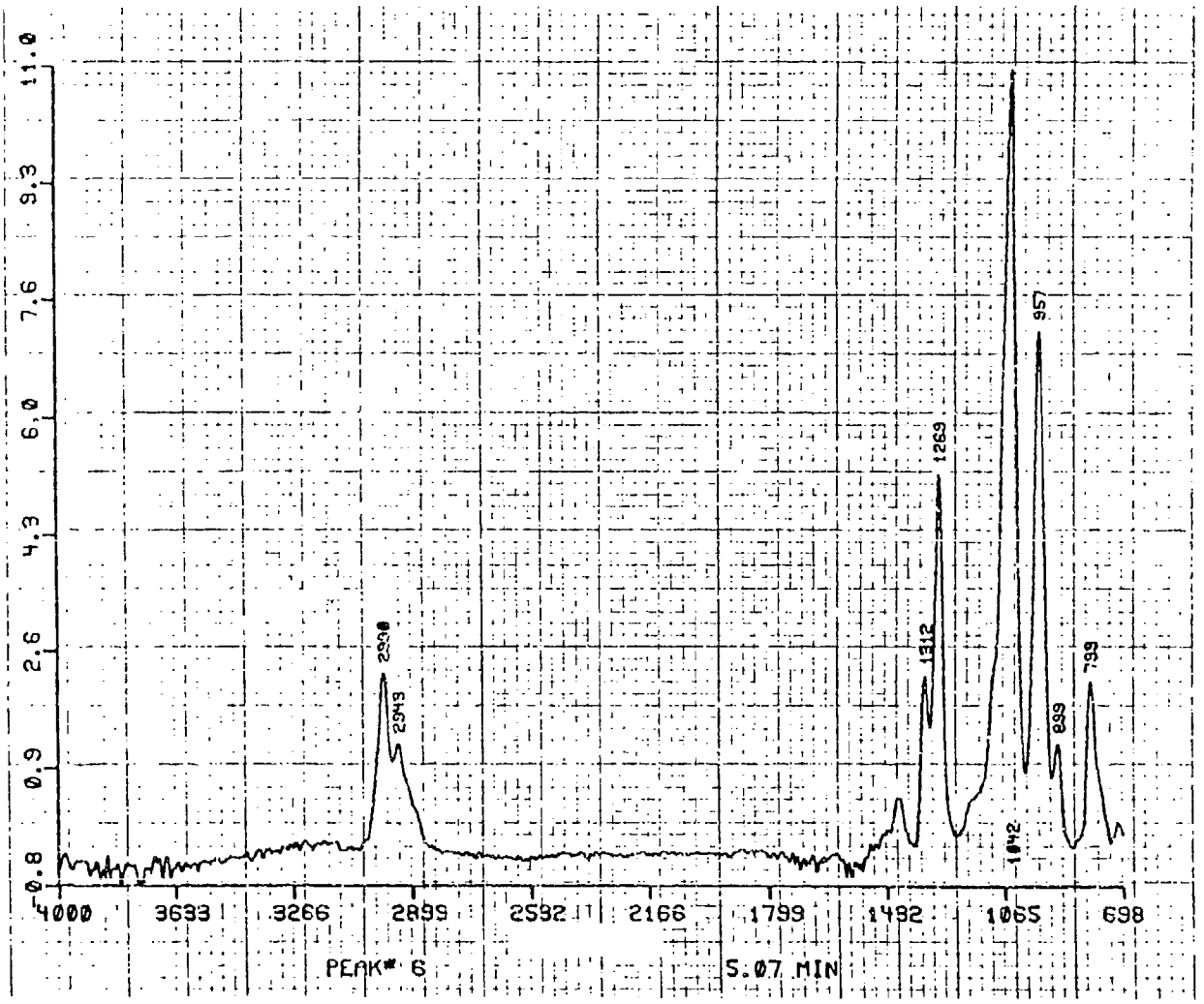

Figure F-2. Peak No. 6, YL

absorbance wavelengths. The digital scan is used to accurately find the peaks' wavelength by the following steps.

1. Find the approximate wavelengths of the sample absorbance bands. A KB sample of 13 ppm was introduced and the following performed:

PRESS : SCAN 8 ENTER

The analyzer prints the approximate peak wavelengths as each THRESHOLD change in transmission is exceeded. (Peaks may be printed if the analyzer goes over a segment change at about 4.5 or 8 μm: these should be ignored. When an x-y recorder is used, the printed wavelengths may be noted on the chart as they are printed out.

2. Find the exact absorbance peak wavelength using DIGITAL SCAN. The gas cell is flushed with clean air. The chosen KB peaks in our example are 8.4, 8.53, 8.55, and 8.8.

A wavelength region bracketing a peak is chosen (8.35 to 8.45 μm would be good in this case).

PRESS : SCAN 5 ENTER

DISPLAY: FROM 8.000

PRESS : NO 8.35 ENTER (start wavelength)

DISPLAY : TO 14.500

PRESS : NO 8.45 ENTER (end wavelength)

PRESS : 7 ENTER

DISPLAY: # OF STEPS 25?

PRESS : NO 30 ENTER (30 steps is a good choice)

DISPLAY : 0 SAMPLE? (ensure zero sample-in this case clean air is Present in sample cell)

PRESS : YES

DISPLAY : (delay) SAMPLE?

PRESS : YES (with sample of component in cell -13.03 ppm KB in this case)

Printer will not list the digital step wavelengths and the corresponding absorbance. The absorbance peak corresponds to the largest absorbance figure.

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3. The first KB peak is now established at 8.440 for this particular MIRAN 980. The procedures outlined in Step 2 are now repeated for other wavelengths of the KB sample and the samples of 18.478 ppm (0.5 µL) YL. In this example, the peak wavelengths were found at 10.450 and 11.120 µm.

4. Parameters for the analysis can now be entered into the MIRAN 980 and calibration can be performed. Data is entered by MEMORY mode, in contrast to the SCAN mode that has been used so far.

PRESS: RESET MEM 3 ENTER

DISPLAY : # WAVES 0?

PRESS: NO 6 ENTER (This is a 2 wavelength analysis)

DISPLAY : # COMPS 0?

PRESS : NO 2 ENTER (2 component analysis)

DISPLAY : ANALYZE TIME 0?

PRESS : NO 6 ENTER (6 is a reasonable analysis time-2 s per wavelength

DISPLAY : REPEAT TIME 0?

PRESS : YES (Analyzer will do 1 analysis and stop)

DISPLAY : MICRONS?

PRESS : YES (We want to work in MICRONS)

DISPLAY : REF WAVE?

PRESS : YES (This analysis will work best with a zero intercept)

DISPLAY : 0 000?

PRESS NO 4.000 ENTER (4.000 is a good general reference wavelength)

DISPLAY : 0.000?

PRESS NO 8 440 ENTER (8.440 is our first KB wavelength)

DISPLAY : 0.000?

PRESS : NO 8.529 ENTER

DISPLAY : 0.000?

PRESS : NO 8.545 ENTER

DISPLAY : 0.000?

PRESS : NO 8.827 ENTER (Our last KB wavelength)

DISPLAY : 0.000?

PRESS : NO 10.450 ENTER (10.45 is the first YL wavelength)

DISPLAY : 0.000?

PRESS : NO 11.120 ENTER (11.120 is the final YL wavelength)

DISPLAY : DATA MODE ABSORB?

PRESS : NO

DISPLAY : CONC?

PRESS : YES (Want to determine concentrations)

DISPLAY : TIME 00:00:00:

PRESS : NO

DISPLAY : ENTER HOURS

PRESS : HOUR OF DAY ENTER

DISPLAY : MINUTES

PRESS : MINUTE ENTER

DISPLAY : SECONDS?

PRESS : SECONDS ENTER

5. Analytical parameters have been entered. The analyzer is now ready to accept calibration sequence to determine KB and YL over a range of 0 to 4 ppm. We used 0.4, 1.0, and 2.0 ppm as our target concentration values. Three-point calibration was favored over five points because of the length of time required to calibrate the unit. The three point calibration method required 1 hr minimum because, unlike the MIRAN 80, the MIRAN 980 must be purged with clean air after each concentration value is measured.

NOTE: Three-point calibration was a problem when the data was put into the Hubaux and Vos computer program. This program requires at least two to three data points below the detection limit of interest to obtain expected minimum values (i.e., values well above noise level of instrument). The parts-per-million values can be produced by closed loop pump techniques or any other method which will generate accurate low concentrations such as diffusion, permeation, or ram-driven syringe method.

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The number of standards must be at least equal to the number of components for zero intercept analysis or an error condition results. For nonzero intercept analysis, at least one additional standard is needed. Either pure or mixture components may be used. If mixtures are used, care must be taken to ensure that the ratios of components are different in all standards. In our example, we used pure components. The calibration process is begun by entering the following:

PRESS : RESET CAL 3 ENTER

DISPLAY : # OF STANDARDS 0?

PRESS : NO 10 ENTER

6. We have to name the components and identify the measurement units (ppm in this case).

PRESS : 4 ENTER

DISPLAY : ****?

PRESS : NO ACRYL ENTER

DISPLAY : ACRYL ****?

PRESS : NO PPM ENTER

DISPLAY : ****?

PRESS : NO STYRN ENTER

DISPLAY : STYRN ****?

PRESS : NO PPM ENTER

7. The analyzer is now ready for calibration, and a STANDARD RUN can be performed.

PRESS : 5 ENTER

DISPLAY : STANDARD 0 READY?

PRESS : YES (With zero sample in this case clean ambient air in the sample cell)

DISPLAY : STANDARD 1 READY?

PRESS : YES

DISPLAY : A10.000?

ENTER : NO (conc) ENTER [Where (conc) is the concentration of the second component in the first sample]

DISPLAY : (delay) STANDARD 2 READY?

PRESS : YES

DISPLAY : A20.000?

Continue gathering data for the remaining calibration samples.

8. Once the standard run is completed, the absorbance and concentration data in the MIRAN 980 memory is converted to the P-MATRIX. The matrix will be used during analysis mode to analyze mixtures of acrylonitrile and styrene vapor.

PRESS : 10 ENTER

DISPLAY : (P-MATRIX)

The matrix is printed automatically, and the printout should be stored for reference purposes.

9. The analyzer is now ready to determine the concentration in ambient air samples. The MIRAN 980 should be rezeroed by drawing a clean (carbon filtered) air sample through the gas cell, then ZERO.

PRESS : RESET ZERO (With clean air in cell)

An ambient air sample can then be drawn through the gas cell and analyzed.

PRESS : ANLYZ

The absorbances and concentrations in ppm of the acrylonitrile and styrene will be automatically printed.

Once the analyzer has been set up and calibrated, ZERO and ANALYZ are the only functions that have to be used.

10. The calibration and matrix information can be stored on a cassette, so that the analysis can be performed again without the need to reenter setup information via the keyboard. To store the information, put a blank cassette in the cassette slot and key the following:

PRESS : RESET TAPE 3 ENTER

DISPLAY : REWINDING

The analyzer will ask for:

LABEL DATE USER CELL NOTE

APPENDIX F

At each stage a reply of up to 11 characters can be entered. The analytical parameters will then be stored.

To read an analysis from tape, load the cassette tape and key in the following:

PRESS : RESET TAPE 2 ENTER

This instruction loads the stored analytical program. The analyzer will print the tape label information (so the operator can verify that the correct tape has been loaded) before loading data. The display will show:

CONTINUE READ?

If the proper label is printed:

PRESS : YES

and the program will be loaded into memory.

This concludes the operations/calibration sequence used for each of the calibrations performed with the MIRAN 980.

Blank

APPENDIX G

CALIBRATION FOR KB AND YL

The MIRAN 980 combines the accuracy and precision of a single beam IR spectrometer with the advantages of microprocessor control. The system is user oriented and so fully automated that complex multi-component quantitative analysis can be performed by any operator who has just minimal knowledge of IR spectroscopy.

Calibratian of the MIRAN 980 for analysis of samples with up to five components can be accomplished in a short time. The calibration Procedure involves selecting the analytical parameters and determining the absorbance of known standard mixtures. An automatic peak picker routine makes it easy to locate the analytical band for analysis. Once the standard mixtures have been prepared and analytical parameters have been chosen, the instrument setup will take about 20 min. Analysis and printout of a single-component sample can be completed in about 15 s; five-component samples are typically completed in 30 s. Data can be presented in any of the three analytical modes, which include Absorbance, Concentration, and Band Ratio.

The microcomputer controls the interactive program that prompts the operator through the choices and functions of the analyzer. It controls the spectrometer, signal averages the measurements, calculates absorbance values, and generates a coefficient matrix to calculate the composition of an unknown mixture. With its full diagnostic routine, the MIRAN 980 is thoroughly reliable and easy to service.

After initial calibration, the analytical program can be stored on magnetic tape and reentered in less than a minute. Then, a complete analysis can be initiated by a few keyboard entries. The analyzer can also scan the background and store this data in memory. As the sample is scanned, the background is automatically subtracted for a Flat Baseline spectrum. An unlimited number of analytical programs and spectra can be retained indefinitely and recalled as often as necessary by the use of a number of tapes.

Detailed Procedure for Analytical Calibration

In this section, the analytical calibration procedure is described. Operator entry functions through the keyboard are defined and summarized.

Step 1 - ANALYTICAL and REFERENCE WAVELENGTHS

Several scan models described below are available to the analyst. Each scan mode provides different information for wavelength selection. The final scan must be a DIGITAL SCAN to precisely define the wavelengths.

SURVEY SCAN - When this scan mode is used, the blackbody curve is superimposed over the sample spectrum.

The sequence of steps for performing a survey scan are:

A. Enter SCAN SPEED — SCAN 3

0-fastest; 99-slowest, (5-10 is typical)

B. Set SEGMENT GAINS — SCAN 4

With no sample in the beam. This is done only once each day or whenever the sample cell is changed.

C. Enter FROM/TO — SCAN 5

Max. number of digits: XX.XXX μm; XXXX.X cm^{-1}

D. SURVEY SCAN the sample — SCAN 6

This sequence of commands provides an infared spectrum of the compounds of interest. See Figure 1. To determine the regions of strong peaks, the Peak Picker Option is used. After completion of the Survey Scan and before the Peak Picker Option, purge the cell with zero air on whatever background gas present.

Peak Scan - When this scan mode is used, the analyzer locates and prints the approximate wavelength position of the band. A digital scan is then Performed to precisely define the wavelength. The transmission threshold to activate the peak picker is previously selected by the operator. Since the instrument looks for a change in transmission, the wavelength is printed after the band is passed. The sequence of steps for performing a peak Picker scan are:

A. Enter SCAN SPEED — SCAN 3

0-fastest; 99-slowest

B. Set SEGMENT GAINS with — SCAN 4

No sample in the beam. This is only once each day or whenever the sample cell is changed.

C. Enter FROM/TO — SCAN 5

Max. number of digits: XX.XXX μm; XXXX.X cm^{-1}. Enter the shorter wavelength first. Example: 4000 to 689 cm^{-1}, 2.5 to 14.5 μm.

D. Enter THRESHOLD — SCAN 11

Threshold range; 3-29% Transmission

E. Scan the BASELINE — SCAN 10

With zero sample or empty cell.

Peak Picker

FROM 2.500M
TO 14.500M
SCAN SPEED 5
PEAK PICKER

3.022	20.8%T
3.397	35.8%T
3.465	44.7%T
3.749	83.4%T
7.244	21.6%T
7.603	25.4%T
7.956	59.3%T
8.971	8.5%T
10.532	13.5%T
12.246	28.7%T
14.269	32.5%T

Digital Scan

FROM 3.370M
TO 3.400M
#OF STEPS 30
DIGITAL SCAN

3.370	0.3855
3.371	0.3961
3.372	0.4039
3.373	0.4095
3.374	0.4141
3.374	0.4194
3.375	0.4247
3.376	0.4301
3.377	0.4342
3.378	0.4359
3.379	0.4391
3.380	0.4413
3.381	0.4439
3.382	0.4451
3.383	0.4463
3.383	0.4473
3.384	0.4471
3.385	0.4477
3.386	0.4485
3.387	0.4487
3.388	0.4495
3.389	0.4493
3.390	0.4480
3.391	0.4468
3.392	0.4453
3.392	0.4439
3.393	0.4429
3.394	0.4404
3.395	0.4392
3.396	0.4379
3.397	0.4365
3.398	0.4346
3.399	0.4326
3.400	0.4307

Table. Peak Picker and Digital Scan Readings of Major IR Bands

F. PEAK PICKER SCAN the sample SCAN 8

Making sure the cell has been filled with sample and closed circulating pump turned off.

After entering the command, "Scan 8," peaks of strongest absorption are printed out as presented in the figure. Upon completion of the Peak Picker routine, the cell is purged. The spectra scan routine is selected to obtain a flat baseline scan before obtaining precise wavelength values to be used for routine analysis and instrument calibration.

Spectra Scan - This scan mode produces a flat baseline scan, subtracting the baseline from the sample spectrum. The sequence of steps for performing a spectra scan are:

A. Enter SCAN SPEED SCAN 3

0-fastest; 99-slowest

B. Set SEGMENT GAINS SCAN 4

With no sample in the beam. This is done only once each day or whenever the sample cell is changed.

C. Enter FROM/TO SCAN 5

Max. number of digits: XX.XXXμm; XXXX.X cm^{-1} Enter the shorter wavelength first. Example: 4000 to 689 cm^{-1} ; 2.5 to 14.5 μm.

D. Scan the BASELINE (purge cell if not clear of sample) with zero sample or empty cell. SCAN 10

E. SPECTRA SCAN SCAN 9

Fill cell with sample before entering this command.

Making sure cell is closed and/or closed loop circulating pump is turned off. (This is not necessary if continuous airflow is used.)

After completion of the spectra scan, a digital scan is performed on the same sample to obtain specific values, which are entered into the MIRAN 980 wavelengths for a particular component. The digital scan can be repeated for each peak chosen from the Peak Picker Routine without having to purge and refill cell. When using this method, one is trying to band the peak to find the wavelength of strongest absorption.

Step 2. PATHLENGTH SELECTION - Determination of the suitable Pathlength for the concentration range of all components to be measured.

Step 3. SLIT SELECTION - a slit of 1 mm is used for gas analysis and most transmission analyses. For greater sensitivity (at expense of lower signal/noise ratio), a slit of 2 mm is always used.

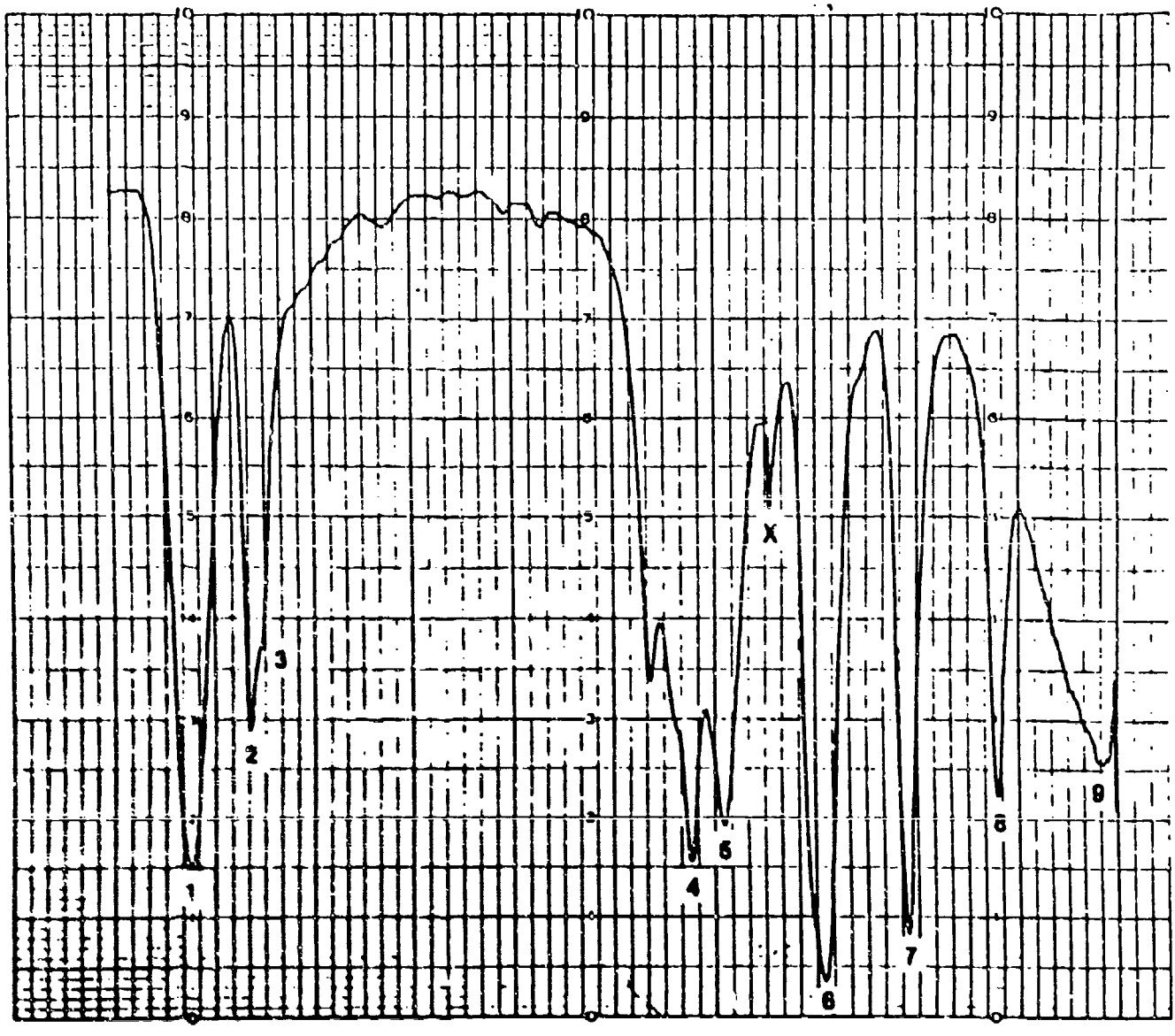

Figure. MIRAN 80 Scan of Isopropanol

Step 4. DIGITAL SCAN - A digitized (incremented) scan between two chosen wavelengths and with a chosen number of steps. This scan mode is used to precisely locate an absorption band. The height of each step is proportional to the derivative of the absorbance. This makes it easy to detect "shoulder" on the side of a strong band. The sequence of steps for performing a digital scan are:

A. Enter SCAN SPEED SCAN 3

0-fastest; 99-slowest.

B. Enter FROM/TO SCAN 5

Each digital scan must be confined to a single segment of the filter. Enter the shorter wavelength first. Acceptable ranges are:

2.45 to 4.449 μm

4081.6 to 2247.6 cm^{-1}

4.45 to 7.949 μm

2247.2 to 1258.0 cm^{-1}

7.95 to 14.6 μm

1257.8 to 684.9 cm^{-1}

Max. number of digits: XX.XXX μm; XXXX.X cm^{-1}. Number of steps: 1-99.

C. Digital SCAN the sample SCAN 7

After collection of all wanted peak data, the cell is purged with zero/background air and the collected data is entered into memory.

Step 5. Enter Memory parameters. (Must reset to enter this mode.)
DEPRESS

MEMORY 3 ENTER

The instrument sequentially advances from item to item and prompts the operator to enter the value of each parameter.

A	#OF WAVES	12 Maximum	MEMORY 4
B	#OF COMPONENTS	10 Maximum	MEMORY 5
C	ANALYZE TIME	0-99	MEMORY 6
D	REPEAT TIME	0-99	MEMORY 7
E	WAVES OR MICRONS	a toggle	MEMORY 8
F	REFERENCE OR NON REF.	a toggle	MEMORY 9
G	ZERO OR NON/ZERO	a toggle	MEMORY 10
H	WAVELENGTHS	12+Ref.Max.	MEMORY 11
I	DATA MODE	Choice of 3	MEMORY 12
J	TIME	hours, minutes, sec	MEMORY 13
K	LOCAL/REMOTE	local or remote option	MEMORY 14

These parameters are required before a calibration of the unit can be obtained. Although this unit can accept up to 12 wavelengths and 10 components, the P-Matrix and Concentration Matrix computation programs cannot be used. If a calibration using the MIRAN 980 is performed the number of wavelengths must not exceed six plus a reference. The number of components cannot exceed three. To include more than 6 wavelengths, an external computer must be used, like that used with the MIRAN 80. The P-Matrix and Concentration Matrix are then entered manually.

Step 6. Enter CALIBRATE parameters and determine ABSORBANCE VALUES at each selected wavelength. (Must reset to enter the Calibrate Mode.)

A.	# Of STANDARDS (18 Maximum)	CAL 3
B.	NAMES AND UNITS	CAL 4
	5 characters max. for names 4 characters max. for units	
C.	STANDARD RUN	CAL 5

The analyzer prompts the operator to introduce each standard (Standard 1 Ready?) and enter the concentration of each component. When all standards have been run, the A-Matrix is printed.

Step 7. List C-MATRIX (Reset the enter command.) CAL 9

Calculate P-MATRIX CAL 10

Step 8. Plot CALIBRATION CURVES for each component. If linearity is a problem, select new analytical parameters, nonzero intercept, or limited concentration range.

Step 9. ANALYZE a known test sample (Reset then enter command.)

ANALYZE

Step 10. Write parameters to TAPE for future use. TAPE 3

This step is also menu driven.

Explanation of features contained within specific key functions: Key function address are:

- Memory
- Calibrate
- Scan
- Tape

MEMORY

1. MENU - A list of all items within this function. The number associated with each item is used to address that item through the keyboard.

2. LIST PARAM - A list all entries that have been programmed within this function.

3. EDIT PARAM - The operator enters the value of each parameter. The instrument sequentially advances from item #4 through item #13.

4. # OF WAVES - The number of analytical wavelengths required for a given analysis. The instrument accepts a maximum of 12 analytical wavelengths.

5. # OF COMPONENTS - The number of components to be measured. The instrument has the capability to analyze up to 10 components; however, a maximum of 5 is recommended.

6. ANALYZE TIME - The instrument takes 64 readings per second for a number of seconds allotted. Longer analysis times mean that the readings are taken over a longer period of time, and thereby lead to a better time weighted average. The numbers available are 0-99 sec.

7. REPEAT TIME - The length of time between sequential analyses. When in "ANALYZE," the instrument makes one set of analyses at the designated wavelengths. Then there is a pause before the next set of absorbance readings. This pause is called the Repeat Time. A Repeat Time of zero results in only one set of data. Repeat Time of 0-60 is actual time in seconds. Repeat time of 61-99 follows equation:

ACTUAL TIMES (MINUTES)	REPEAT TIME	ACTUAL TIME
=2 (REPEAT TIME -60)	1	1 sec
	.	.
	.	.
	.	.
	60	1 min
	61	2 min
	62	4 min
	63	6 min
	64	8 min
	65	10 min
	.	.
	.	.
	.	.
	99	78 min

8. WAVES/MICRONS - The operator chooses whether the wavelengths will be in cm-1 or microns. It is a toggle function. Enter MEMORY 8 ENTER and it will ask "MICRONS?" in the digital display. If that is desired, enter

"YES". If cm-1 is desired, enter "NO." Then the display will read cm^{-1}, enter "YES." When the "YES" is entered, the chosen parameter will be Printed.

9. REF/NON REF - The operator chooses to use a reference wavelength or non-reference analysis. The choice of referenced analysis will eliminate Possible instrument drift by subtracting the absorbance at the referenced wavelength from the absorbance at the analytical wavelength.

10. ZERO/NON-ZERO INTERCEPT - The NON-ZERO intercept is often used for samples whose calibration curves are markedly nonlinear. The analyst makes a choice between extending the concentration range or improving the accuracy.

11. WAVELENGTHS - A list of wavelengths in memory. If a reference wavelength is used, it must be listed first. Up to 12 analytical wavelengths and a reference wavelength can be entered.

12. DATA MODE - There are three data modes:

ABSORBANCE

CONCENTRATION

BAND RATIO

There is choice of data mode. By pushing "NO," the display will show each of the choices. Select a mode by pushing "Yes."

13. TIME - The real time in hours, minutes, and seconds.

14. LOCAL/REMOTE - When a remote terminal is used, the operator chooses whether data will be presented locally on the analyzer, remote, or both.

CALIBRATE

1. MENU - A list of all items within this function. The number associated with each item is used to address that item through the keyboard.

2. LIST PARAM - A list of all entries that have been programmed within this function.

3. # OF STANDARDS - The number of standard samples used for a quantitative analysis. For a system where the calibration curve results in a zero intercept, the number of standards required for quantitative analysis must be equal to the number of analytical wavelengths. More standard samples may be used if desired.

For a system with non-zero intercept, there must be at least one more standard sample than the number of analytical wavelengths. The maximum number of standard samples is 18.

4. NAMES AND UNITS - The names of the components being analyzed are entered. This is used in the RATIO and CONCENTRATION modes. There are

five characters available for the NAME and four characters available for the UNITS. Letters may be entered by using the LEFT/RIGHT shift keys that are located on each side of the "o."

5. STANDARD RUN - This is the development of the Absorbance matrix (A-matrix). First the instrument automatically zeros itself (Standard 0). The solvent or background is placed into the beam. Then, depending on the number of standards, the instrument will ask for the standards by number (STANDARD READY 1?). The sample is placed into the beam and absorbance data gathered. When the sample is ready and has been into the proper position, enter "YES" and the instrument will analyze that standard. The display will ask for each sample when it has completed readings of the Previous sample. The concentration of each component is entered and this builds the concentration (C-matrix). The A-matrix will be printed out when all standards have been run.

6. EDIT A-MATRIX - If data is available from a previous analysis it may be entered here in the EDIT step.

7. LIST A-MATRIX - The instrument will bring out the matrix that has been programmed into memory through the STANDARD RUN, or the EDIT step.

EDIT C-MATRIX - (see #6 - EDIT A-MATRIX)

9. LIST C-MATRIX - (see #7 - LIST A-MATRIX)

10. CALCULATE P-MATRIX - After the A-Matrix has been entered or generated through the STANDARD RUN, and the C-Matrix has been entered, then the P Matrix can be calculated.

11. EDIT P-MATRIX - (see #6 - EDIT A-MATRIX)

12. LIST P-MATRIX - (see #7 - LIST A-MATRIX)

13. CALIBRATE SERVO - Known absorption bands of polyethylene and polystyrene films are used to calibrate the filter and servo system. The background must be stored first. This is an automatic test, but the correct wavelength positions may be entered manually.

14. DETECTOR CHECK - There are two tests which check detector phase and check for adequate energy throughout. The Li Ta O detector is a solid state crystal which has two polarities. Test #1 determines if the detector is in phase A or B. If the detector preamplifier assembly is not aligned or if a system component's failure causes low energy, test #2 will fail and the following message will be printed:

CHECK DETECTOR

SCAN

1. MENU - A list of all items within the function. The number associated with each item is used to address the item through the keyboard.

2. LIST PARAM - A list of all entries that have been programmed within this function.

3. SCAN SPEED - A function of the speed at which the filter wheels scan the spectrum. Slower scan speeds lead to greater accuracy. The following table shows the actual time for a spectral scan (2.5 - 14.5 μm) at various scan speeds.

Scan Speed of 1 is generally used for digital scan. Scan Speed of 10 is generally used for peak pick scan.

SCAN SPEED	ACTUAL TIME
1	1 min
5	3 min
10	5 min
20	9 min
40	18 min
80	33 min
90	37 min
99	40 min

4. SEGMENT GAINS - This optimizes the peak transmission in each of the segments of the filter wheel. These data are stored in memory.

5. FROM/TO/STEPS - The operator selects the wavelength to begin and end a scan procedure. If the analysis is in um, the beginning wavelength must be the smaller number (i.e. 2.5 -14 μm). If the analysis is in cm^{-1}, the beginning wavelengtn must be the larger number.

Acceptable range: 2.45-14.6 μm. Maximum number of digits: XX.XXX μm; XXXX.X cm^{-1} Number of steps: 1-99.

6. SURVEY SCAN - A qualitative scan between two chosen wavelengths. When the scan mode is used, the blackbody curve is superimposed over the sample spectrum.

7. DIGITAL SCAN - A digitized (incremented) scan between two chosen wavelengths and with a chosen number of steps. This scan mode is used to Precisely locate an absorption band.

Each digital scan must be confined to a single segment of the filter. Acceptable ranges are:

2.45 - 4.449 μm
4.45 - 7.749 μm
7.95 - 14.6 μm

8. PEAK PICKER - The analyzer locates and prints the approximate wavelength position of a band. The Transmission Threshold to activate the peak picker is previously selected by the operator. Since the instrument looks for a change in transmission, the wavelength is printed after the band is passed.

In order to use the peak picker, the baseline must first be stored in memory.

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9. SPECTRA - This mode produces a flat baseline scan, subtracting the baseline from the sample spectrum.

10. BASELINE - Scans the background and stores data in memory for subtraction from scans 8 or 9.

11. THRESHOLD - The transmission desired for the Peak Picker scan. High thresholds work well for strong band. A threshold of 8% is automatically set when the analyzer is powered up Threshold Range: 3-29% Transmission.

TAPE

1. MENU - A list of all items within this function. The number associated with each item is used to address that item through the keyboard.

2. READING - All paramenters that were stored on tape are transferred to instrument memory. When tape 2 is initiated, the cassette label is Printed out and the display shows: CONTINUE READ? The label consists of:

LABEL

DATE

USER

CELL

NOTE

This identifies the program stored on the cassette. Press "YES" to have the date read from the cassette. If this is not the desired program, press "NO" and the tape will rewind. When the tape has been read, the printer will print READY and the display will show TAPE.

NOTE: To confirm that the parameters have been transferred to memory, press:

RESET MEMORY 2 ENTER

3. WRITING - All parameters in instrument memory are stored on tape for future use. The tape must be labeled to define the analysis. The label consists of :

LABEL

DATE

USER

CELL

NOTE

APPENDIX G

Each item may have up to 11 characters. Writing of data to the cassette begins after entering the NOTE. If there is no information to Put in NOTE, simply press ENTER when it appears on display. During the writing procedure, the display shows what is happening:

WRITING

REWINDING

VERIFYING

The verifying step checks that all data has been correctly loaded on the tape.

APPENDIX C

Blank

APPENDIX H

SETUP OPERATIONAL CHECKOUT OF THE MIRAN 80

This section presents specific instructions on how to set-up and operate the MIRAN 80.

A. Theory

Infrared (IR) rays are heat rays overlapping the long wave end of the visible spectrum, between the wavelengths of 2.5 and 14.5 μm. These rays do not affect the eye and are measurable by thermal (pyroelectric) detection. Molecules, when subjected to IR rays, absorb some of their energy at wavelengths that are characteristic to each molecule. Thus, by knowing at which characteristic wavelengths molecules absorb, identification can be made of the compound; and by knowing how much absorption has taken place, the concentration of the compound can be determined.

The MIRAN 80 uses this IR technique for quantitative measurement of the concentrations of mixtures of components. The MIRAN 80's IR energy is generated by an internal source. This energy is concentrated by a mirror and focused so that it passes through the material in the sample cell and strikes a pyroelectric detector. The amount of molecular absorption is dependent on the length of contact with the IR energy. Therefore, the pathlength of the infrared rays through the sample cell of the MIRAN is made variable by a series of reflecting mirrors from 0.75 to 20.25 μm, so that varying degrees of sensitivity may be obtained. The MIRAN has a circular variable filter through which the IR rays pass. The filter rotates to a wavelength, preselected as being characteristic to an individual compound. Absorption is measured at each selected wavelength by the pyroelectric detector; the signals are electrically Processed; and concentrations calculated for the compounds associated with the selected wavelength.

B. Calibration Methods

1. Closed Loop Construction

The first step toward actual calibration of the MIRAN 80 is the determination of analytical wavelengths for the compounds of interest. (If this has already been accomplished, proceed to Section 5. To determine the precise analytical wavelengths, a closed loop system for sample analysis is employed (see Figure).

1.1 Construction of Closed Loop System follows: (All connectors and tubing for loop itself are stainless steel).

1.2 Extending from the inlet port is a short piece of tubing with a tee swagelock fitting connected to the other end. The remaining two ends of the tee fitting are connected to the output port of the circulating pump and a pressure gauge, respectively. An elbow with a toggle switch (S2) at one end is fitted to the other end of the pressure gauge.

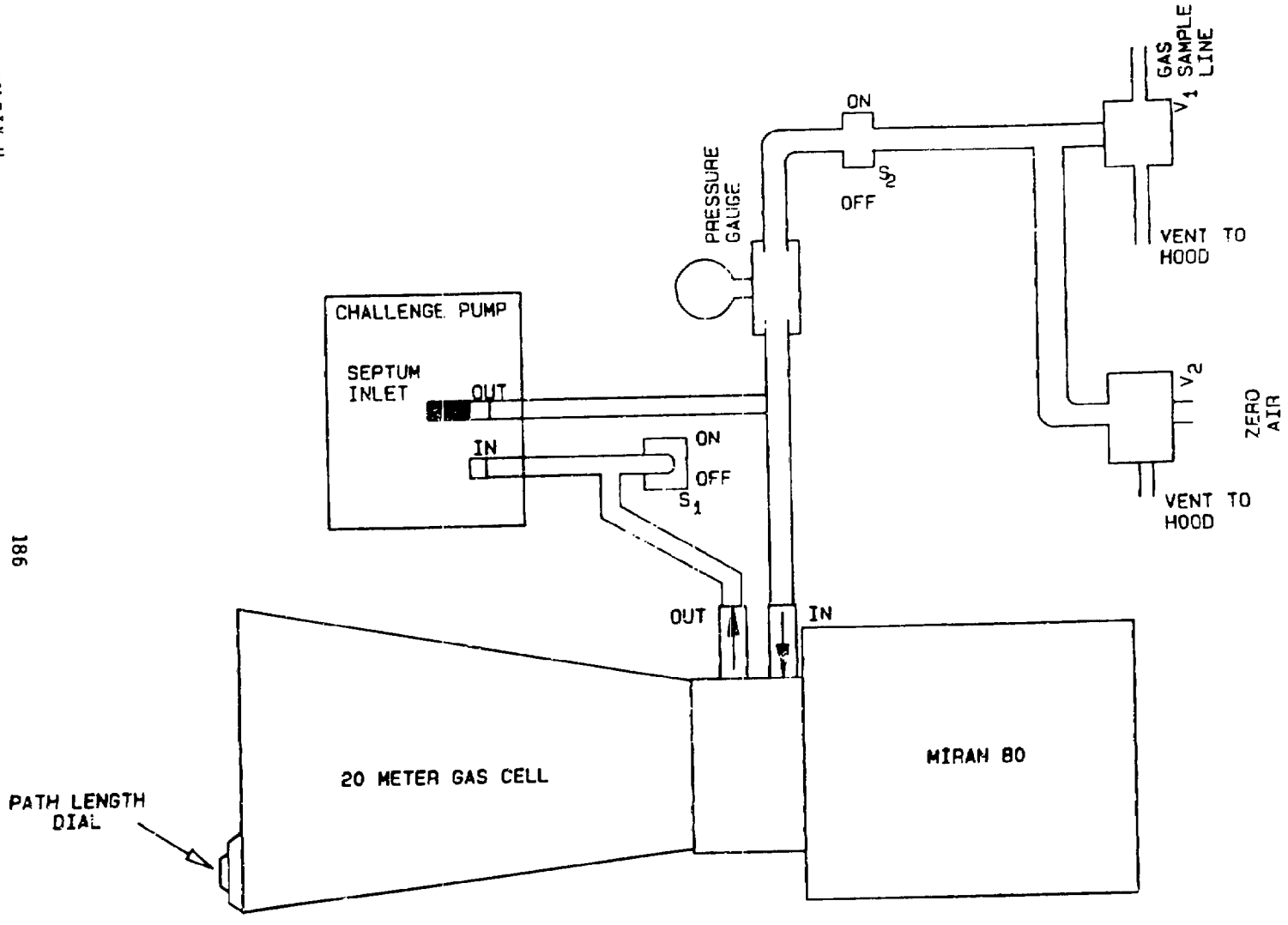

Figure. Closed Loop System

1.3 The other end of the toggle switch contains a short piece of tubing with a tee connector at the end.

1.4 To one end of the tee connector, a two-way switching valve (VL) is added.

1.5 The other end of the tee connector contains a short piece of tubing with an elbow.

1.6 The intake port of the challenge pump is connected to a tee connector that has a toggle switch (S1) at one end. The exit port of the MIRAN is on the other end of the tee connector.

1.7 The output port of the challenge pump is fitted with a tee connector equipped with a septum at one end for syringe injection.

1.8 The other end of the tee connector is fitted with a piece of stainless steel tubing that connects to the tee fitting described in section 1.2.

1.9 The remaining two ports on switching valve (V1) are attached to the gas sampling line and a hood vent respectively.

1.10 Switching valve two (V2) is used for purging MIRAN with zero air. The switch that does not connect to the closed loop is used for venting to the hood.

2. Injection Techniques

Now that the MIRAN is fully constructed, the next step in its operation is the injection of samples of known concentration.

2.1 Gas injection: Obtain a source of the pure component gas. Attach a septum inlet tee to the source. Teflon tubing should run from the tee to the bottom of a flask. The flask is filled with a solution that would not react violently or yield dangerous products on contact with the gas. Allow the gas to purge the Teflon line. This can be monitored by observing the gas bubbling through the solution. After sufficient purging, draw a sample from the septum inlet using a gas-tight microliter syringe. (These syringes require meticulous care, as they are prone to plugging easily.) Inject the sample into the closed loop calibration system. The resulting concentration in parts-per-million of the component gas in the system is calculated as follows:

$$\text{Concentration } (C_{ppm}) = \frac{Vi}{Vs} \qquad (1)$$

where

Vi = the microliters of gas injected

Vs = the 5.64 L of diluent volume in the closed-loop system.

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2.2 Liquid injection: The concentration in parts-per-million of a pure component liquid injected into the closed-loop system is calculated as follows:

$$\text{Concentration } (C_{ppm}) = \frac{ViD}{M} \times \frac{RT}{P} \times \frac{10^3}{Vs} \qquad (2)$$

where D = liquid density in g mL^{-1}

R = 0.08206 atm^{-1} degree K mole (the universal gas constant)

T = temperature in degree K

P = pressure in atmospheres

M = molecular weight of sample in g $mole^{-1}$

V_i = microliters of sample injected

V_S = 5.64 L of diluent volume in the closed loop system

The higher the boiling point of the liquid, the longer one should wait for the sample to volatilize in the system before performing any analysis.

3. Preparation of Instrument for Wavelength Determination

3.1 Place the MIRAN in operation as described in Section 1.1.

3.2 Turn MIRAN 80 on, allow 1 hour warm up.

3.3 Shut circulating pump off, wait a few seconds for the pressure in the loop to equilibrate with atmospheric pressure, then turn VI to allow for challenge pump purge. Purge for 1 minute, shut pump off, let Pressure equilibrate, then close loop.

3.4 Select a slit width. This is set manually by turning a screw on the side of the instrument. There are three choices of slit width (0.5, 1, and 2 mm). The narrower the slit, the better the resolution but with less available energy. The 1 mm width is usually selected.

3.5 Set cell pathlength. The cell pathlength is variable in 1.5 m increments from 0.75 to 20.25 m. (Do not use the 21.25 m setting.) Select a pathlength according to the sensitivity desired. The longer the pathlength, the greater the sensitivity. The procedure for setting the desired pathlength is as follows:

3.5.1 Release the lock on the pathlength dial, and turn the dial to 0.00.

3.5.2 Open the instrument memory by key strokes:

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3.5.2.1 Clear.

3.5.2.2 8531616.

3.5.2.3 Blue.

3.5.2.4 Blue (memory access light on).

3.5.3 Set the gains across the filter segments by key strokes:

3.5.3.1 Clear.

3.5.3.2 Blue.

3.5.3.3 E.

3.5.3.4 Wait for ready light before proceeding.

3.5.4 Set a wavelength of 3.500 μm by key strokes:

3.5.4.1 Clear.

3.5.4.2 3.5.

3.5.4.3 Yellow

3.5.4.4 4.

3.5.5 Set a gain of three by the keystrokes:

3.5.5.1 Clear.

3.5.5.2 3.

3.5.5.3 Blue.

3.5.5.4 4.

3.5.6 Disable printer by keystrokes:

3.5.6.1 Clear.

3.5.6.2 0.

3.5.6.3 Yellow.

3.5.6.4 6

3.5.7 Start instrument analyzing by the keystrokes:

3.5.7.1 Clear.

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3.5.7.2 Yellow.

3.5.7.3 9.

3.5.8 Turn the pathlength dial fully counterclockwise.

3.5.9 Observe the energy bar graph to the right of the keyboard. The level of energy will be very low.

3.5.10 Set an RDTM of 1 by keystrokes:

3.5.10.1 Clear.

3.5.10.2 1.

3.5.10.3 Blue.

3.5.10.4 0.

3.5.11 Set instrument for digital readout of energy bar graph using key strokes.

3.5.11 1 Clear.

3.5.11.2 Yellow.

3.5.11.3 Blue.

3.5.11.4 A.

3.5.11.5 The digital readout will now display the transmission voltage. This is more accurate than simply viewing the bar graph for setting the pathlength dial.

3.5.12 Slowly turn the pathlength dial clockwise while watching the energy bar graph until you see the level of energy increase and then fall again. A sharp peak of energy should be evident. If the gain is set too high, you will not be able to see a sharp peak of energy. In this case turn the pathlength dial to where you estimate the energy peak occurs and return to steps 3.5.3-3.5.3.4. Then proceed to step 3.5.7.

3.5.12.1 If this does not correct the problem, return to 3.5.5 and input a gain of 2 in place of 3.

3.5.13 The first point of maximum energy occurs somewhere around dial setting 0.75 meters. By continuing to turn the pathlength dial clockwise, you will observe the energy rise and fall repeatedly, corresponding to each successive pathlength. The second energy peak, therefore, corresponds to a pathlength of 2.25 m and occurs somewhere around dial setting 1 and so on.

3.5.14 Turn the pathlength dial fully counterclockwise again.

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3.5.15 Observe the sequence of pathlengths printed next to the pathlength dial. Count the number of pathlengths required to reach the one desired.

3.5.16 Turn the pathlength dial clockwise and count the energy peaks until you have reached the energy peak corresponding to the desired pathlength. At this point, back the dial off a bit until the energy drops slightly, then readvance the dial to the energy peak. You must approach the energy peak from lower dial readings to avoid mechanical backlash.

3.5.17 For wavelength detemination, a pathlength of 0.75 m, the first energy peak, will be used. Observe both the energy bar graph and the digital readout to set the pathlength. The digital readout should be maximized on the peak.

3.5.18 Once the pathlength dial has been properly set at the energy peak corresponding to the desired pathlength, lock the dial and record the dial setting in the instrument log.

3.6 Ensure that the instrument is operating in microns and not cm^{-1} by observing indicator lights next to the keyboard. If operation in cm^{-1} is indicated, change to microns by key strokes:

3.6.1 Clear.

3.6.2 Yellow.

3.6.3 W. μ/cm^{-1} 7.

3.7 The number of components (NC) is used by the MIRAN to initiate matrix calculations. These calculations are not needed during calibration. Therefore, set the number of components to 1 by key strokes:

3.7.1 Clear.

3.7.2 1.

3.7.3 Blue.

3.7.4 3.

3.8 Set the filter segment gains:

3.8.1 Clear

3.8.2 Blue.

3.8.3 E.

3.8.4 Wait for ready light before proceeding.

3.9 Tell the computer to enter analysis 1 by key strokes:

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3.9.1 Clear.

3.9 2 1.

3.9.3 Yellow.

3.9 4 ANAL. NO.

3.10 Lock memory by the following key strokes:

3.10.1 Clear.

3.10.2 8531616.

3.10.3 Blue.

3.10.4 Blue (memory access indicator light will go off).

4. Wavelength Selection

(This section may be skipped if wavelengths have already been selected). It is necessary to select one characteristic infrared absorption band in the range of 2.5 to 14.5 μm for each component to be analyzed. It is also necessary to select a reference area that shows no absorption in the presence of any of these components. Selection must also take into account the absorption bands of possible interfering compounds. Initial selection is made from a comparison of published spectra or double-beam spectra determined on actual samples. Confirmation of proper band selection is accomplished by running analog scans of components on the MIRAN 80. The tasks are performed as follows:

4.1 Analog scan procedure used to determine peak and reference.

4.1.1 Connect a strip chart recorder (0-10 V as 0-100% T) to the terminal outputs marked "recorder" on the instrument. Set chart speed to approximately 2 in./min.

4.1.2 Unlock memory by key strokes:

4.1.2.1 Clear.

4.1.2.2 8531616.

4.2.2.3 Blue

4.1.2.4 Blue (memory access light on).

4.1.3 Enter a scanning speed of 11 minutes by key strokes:

4.1.3.1 5.

4.1.3.2 Blue.

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4.1.3.3 D.

4.1.4 Lock memory.

4.1.4.1 Clear

4.1.4.2 8531616.

4.1.4.3 Blue.

4.1.4.4 Blue (memory access light off).

4.1.5 Enter a starting wavelength of 2.5 μm by key strokes.

4.1.5.1 2.5.

4.1.5.2 Yellow.

4.1.5.3 W START.

4.1.6 Enter an ending wavelength of 14.5 μm by key strokes.

4.1.6.1 14.5.

4.1.6.2 Yellow.

4.1.6.3 W. STOP

4.1.7 Set 0% T. (Turn recorder ON, short the two input terminals on recorder and set chart zero).

4.1.8 Set 100% T. (Remove short from recorder terminals and use attenuator to set chart 100%).

4.1.8.1 It is well at this point to make a background run without a sample. This ensures that the optical path is clean and gives a Picture of the background.

4.1.9 Start scan by key strokes:

4.1.9.1 Yellow.

4.1.9.2 SCAN.

4.1.10 The display will read out actual wavelength values during the scan. It is necessary to mark the wavelengths displayed on the recorder chart periodically. The filter wheel in the instrument has three segments, therefore, there will be two spikes in the trace as the wheel goes from one segment to the next. The spikes appear at 4.45 and 7.95 μm. There is also overlapping of the segments near the spikes that can be seen on the digital display. At the end of the scan, the display will read 0. Turn recorder chart drive off. This is the background analog scan. To run an analog scan on individual components, proceed as follows:

4.1.11 Inject a sample through the septum inlet and let recirculate for 2 min. (Refer to Section 2.)

4.1.12 Turn recorder chart drive on.

4.1.13 Initiate a scan.

4.1.13.1 Yellow.

4.1.13.2 SCAN.

4.1.14 At the end of the scan, the display will read 0. Turn recorder off.

4.1.15 Purge system with clean air for 5 min, then reclose system. (If in doubt whether all sample has been cleared from cell, initiate another scan and compare it to the background scan.)

Compare scans obtained and check the published spectra of possible interfering compounds. Select the strongest and sharpest infrared absorption band (corresponding to a minimum % T on the recorder trace) that is characteristic to the individual component. Also select a reference wavelength. It should be in a flat area of the scans, showing virtually no aborption above background during any of the scans (3.9 μm is a recommended reference wavelength for gaseous analysis.).

4.2 Digital scan procedure: (Special Flat Baseline Short Scan) A digital scan over each selected infrared absorption band is used to Precisely locate the wavelength corresponding to maximum absorbance. Taking care that the scan interval does not cross the filter gaps at 4.45 and 7.95 μm the digital scan is performed as follows:

4.2.1 Ensure that the cell has been purged and the system reclosed.

4.2.2 Estimate, from the analog scan of this component, the wavelength corresponding to the beginning of the selected band. Enter this starting wavelength by the following key strokes:

4.2.2.1 Clear.

4.2.2.2 Starting wavelength (microns).

4.2.2.3 Yellow.

4.2.2.4 W. START.

4.2.3 Estimate, from the analog scan of this component, the wavelength corresponding to the ending of the selected band. Enter this stopping wavelength by the following key strokes:

4.2.3.1 Clear.

4.2.3.2 Stopping wavelength (microns).

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4.2.3.3 Yellow.

4.2.3.4 W. STOP.

4.2.4 Set a digital scan of 10 steps by key strokes:

4.2.4.1 Clear.

4.2.4.2 10.

4.2.4.3 Yellow.

4.2.4.4 The key marked "NO. STEPS."

4.2.5 Store background. Instrument will print and store absorbances in 10 steps over the range selected to be used as zeroes for the digital scan.

4.2.5.1 Clear.

4.2.5.2 Yellow.

4.2.5.3 3.

4.2.5.4 Wait for ready light before proceeding.

4.2.6 Inject sample into the system. Wait 2 min for the sample to recirculate.

4.2.7 Scan sample.

4.2.7.1 Clear.

4.2.7.2 Yellow.

4.2.7.3 A.

4.2.8 Upon completion of the digital scan, the MIRAN 80 will print out 10 wavelengths evenly spaced over the selected interval along with the relative absorbances at each. Locate the wavelength having the largest absorbance. Initiate a new digital scan as follows:

4.2.9 Purge cell for 5 min and reclose.

4.2.10 Enter as a new starting wavelength, the wavelength directly before the wavelength of largest absorbance in the previous digital scan.

4.2.10.1 Clear.

4.2.10.2 Starting wavelength (microns).

4.2.10.3 Yellow.

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4.2.10.4 W. START.

4.2.11 Enter as a new stopping wavelength, the wavelength coming directly after the wavelength of largest absorbance in the previous digital scan.

4.2.11.1 Clear.

4.2.11.2 Stopping wavelengtlh (microns).

4.2.11.3 Yellow.

4.2.11.4 W. STOP

4.2.12 Store new background.

4.2.12.1 Clear.

4.2.12.2 Yellow.

4.2.12.3 3.

4.2.12.4 Wait for ready light before proceeding.

4.2.13 Inject sample into the system. Wait 2 min for the sample to recirculate.

4.2.14 Scan sample.

4.2.14.1 Clear.

4.2.4.12 Yellow.

4.2.14.3 A.

4.2.15 This second digital scan should be sufficient to isolate the exact wavelength corresponding to maximum absorbance over the selected absorption band.

If necessary, however, the scan interval may be further narrowed by performing additional digital scans based on previous digital scan data. The wavelength identified in this procedure should be accurate to 0.0005 μm.

Once satisfied with a wavelength selection for this component, purge the system with clean air for 5 min, then reclose. Perform digital scans, and determine wavelengths for each desired component.

4.3 Results of scans: Upon completion of the analog and digital scans, the following should have been chosen:

4.3.1 One reference wavelength.

4.3.2 One analytical wavelength for each desired component.

4.4 After the wavelength determination is complete, the closed loop system may be removed.

5. Determination of Absorbance Measurements

Note: Because the instruments will be calibrated in the Plant area, the MIRAN 80 should not abe configured as diagramed in the figure in section 1.

The setup diagramed in that section is designed for closed loop or gas generated samples only. An alternate method for introducing open environment samples has not been explored by this laboratory.

5.1 Unlock memory.

5.1.1 Clear.

5.1.2 8531616.

5.1.3 Blue.

5.1.4 Blue (access light on).

5.2 Enter the selected reference wavelength (first) followed by the selected analytical wavelengths (in numerical order) into the MIRAN 80 by the following key strokes:

5.2.1 Clear.

5.2.2 1.

5.2.3 Blue.

5.2.4 4.

5.2.5 Reference wavelength (microns).

5.2.6 Blue.

5.2.7 5.

5.2.8 First analytical wavelength (microns).

5.2.9 Blue.

5.2.10 5.

5.2.11 Next analytical wavelength.

5.2.12 Blue.

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5.2.13 5.

5.2.14 Repeat strokes 5.2.11 - 5.2.13 for each additional wavelength.

5.3 Enter the total number of wavelengths (including reference) by key strokes:

5.3.1 Clear.

5.3.2 Total number of wavelengths.

5.3.3 Blue

5.3.4 2.

5.4 Set the number of components to one.

5.4.1 Clear.

5.4.2 1.

5.4.3 Blue.

5.4.4 3.

5.5 Selecte a RDTM (individual reading time at each wavelength) of approximately 1 s by key strokes:

5.5.1 Clear.

5.5.2 1.

5.5.3 Blue.

5.5.4 0.

5.6 Select a ZRTM (number of analysis cycles between auto re-zeroing). A high number is used to prevent auto zeroing. Use the key strokes:

5.6.1 Clear.

5.6.2 225.

5.6.3 Yellow.

5.6.4 Yellow.

5.7 Set PGTM (purge time) to give the shortest purge possible.

5.7.1 Clear.

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5.7.2 1.

5.7.3 Blue.

5.7.4 Yellow.

5.7.5 5.

5.8 Lock memory.

5.8.1 Clear.

5.8.2 8531616.

5.8.3 Blue.

5.8.4 Blue (memory access light off).

5.9 Ensure that the 20-m gas cell has been purged for 5 min.

5.10 Set the wavelength gains:

5.10.1 Clear.

5.10.2 Yellow.

5.10.3 SET GAIN.

5.10.4 Note: The instrument will print "zero."

5.10.5 Wait for ready light before proceeding.

5.11 Set the wavelength zeroes.

5.11.1 Clear.

5.11.2 ZERO.

5.11.3 Note: The instrument will print "ZERO."

5.11.4 Wait for ready light before proceeding.

5.12 Carry out absorbance measurements at the selected wavelengths with a clean cell:

5.12.1 Clear.

5.12.2 ANALYZE.

Wait for the instrument to complete an analysis cycle. At the end of each analysis cycle, the instrument will have printed out the absorbance at the reference wavelength followed by the absorbances at each analytical

wavelength and one concentration (ppm) value. The instrument will then return to the reference wavelength and start another cycle. Cycles are repeated indefinitely until the instrument is cleared. Look at the printout from the first analysis cycle. All absorbance readings should be 0.0005 or less. If this is not the case, return to step 5.11.

5.13 Using the KINTEK standards generator or other permeation generator, calibration gas mixtures can now be introduced into the gas cell.

5.14 Note: The MIRAN 80 should be calibrated at the same pathlength that will be used for sampling. Selection of pathlength is described in section 3.5.13.

Flow rates from the standards generator should be great enough to allow for a 1 ppm sample to be drawn off through the gas cell. (Note: flow through the gas cell must not exceed the flow output from the generator.) Only one compound at a time should be introduced to the cell.

5.15 Start flow of calibration gas, allow the instrument to sample for ten complete analysis cycles. Starting with the fifth cycle, the absorbance readings should be stable.

5.16 Following the 10th analysis cycle, switch the generator to "zero/standby" and allow the MIRAN 80 to analyze at least 10 complete cycles. A fairly stable background absorbance should be observed by the fourth or fifth cycle.

5.17 Clear the analysis function:

5.17.1 Clear.

5.18 The "corrected" response of the instrument should be calculated as follows:

5.18.1 Average the absorbance values of each wavelength for analysis cycles 5-10.

5.18.2 Average the absorbance values of each wavelength for purge cycles 5-10.

5.18.3 Obtain "corrected" absorbance readings by subtracting the purge absorbance averages from the analysis averages. This gives a "corrected" absorbance for each of the four wavelengths.

5.19 Repeat steps 5.14 - 5.18.3 using the same compound and the same concentration until repeatable corrected" absorbances are obtained.

5.20 Repeat steps 5.14 - 5.18.3 for each additional compound.

5.21 Calibration concentrations should be in the working range of the analysis to be performed.

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6. FORTRAN Program

6.1 Input: Form two tables from the absorbance data collected, one giving the absorbance at the analytical wavelength for each sample (disregard reference wavelength and its absorbance) and the other giving the concentration of each component in each sample. A three wavelength-three component example is given in Tables 1 and 2.

Table 1. Absorbance Matrix

Sample	Wavelength 1	Wavelength 2	Wavelength 3
1	A1	A2	A3
2	A4	A5	A6
3	A7	A8	A9

Table 2. Concentration Matrix

Sample	Component 1	Component 2	Component 3
1	C1	C2	C3
2	C4	C5	C6
3	C7	C8	C9

A FORTRAN program using fixed point math is now used to solve an inverted absorption coefficient (P) matrix and corresponding decimal shift number and plus/minus signs (PLUMS).

This FORTRAN program is provided in Appendix I. Given the above two tables, the program can be run on a personal computer based on "zero intercept" matrices.

6.2 FORTRAN output entry into the MIRAN 80:

6.2.1.1 Clear.

6 2.1.2 8531616.

6.2.1.3 Blue.

6.2.1.4 Blue (access light on).

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6.2.2 Insert "P-Matrix for MIRAN 80" into memory. (Start at top left and read across).

6.2.2.1 Clear.

6.2.2.2 1.

6.2.2.3 Blue

6.2.2.4 4.

6.2.2.5 First matrix element.

6.2.2.6 Blue.

6.2.2.7 6.

6.2.2.8 Second matrix element.

6.2.2.9 Blue.

6.2.2.10 6.

6.2.2.11 Continue until all entries are made.

6.2.3 Enter "decimal shift number".

6.2.3.1 Clear.

6.2.3.2 Decimal shift number.

6.2.3.3 Blue.

6.2.3.4 A.

6.2.4 Enter "PLUMS signs."

6.2.4.1 Clear.

6.2.4.2 1.

6.2.4.3 Blue.

6.2.4.4 4.

6.2.4.5 1st Plum No.

6.2.4.6 7.

6.2.4.7 2nd Plum No.

6.2.4.8 7.

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6.2.4.9 Continue until all entries are made.

6.3 Check of matrix entry into memory:

6.3.1 Clear.

6.3.2 Yellow.

6.3.3 Prt Mat.

6.4 Instrument will print all matrix values, followed by the "PLUMS." Matrix values should be printed in the same order of entry.

6.5 Lock memory.

6.5.1 Clear.

6.5.2 8531616.

6.5.3 Blue.

6.5.4 Blue (memory access light off).

7. Analytical Measurements. The instrument is now calibrated and needs only to be given operating parameters to begin analyzing unknowns.

7.1 Unlock memory:

7.1.1 Clear.

7.1.2 8531616.

7.1.3 Blue.

7.1.4 Blue (memory access light on).

7.2 Enter the number of wavelengths:

7.2.1 Clear.

7.2.2 Number of wavelengths. (Total number including reference.)

7.2.3 Blue

7.2.4 2.

7.3 Enter the number of components:

7.3.1 Clear.

7.3.2 Number of components. (Number of compounds to be analyzed.)

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7.3.3 Blue.

7.3.4 3.

7.4 Enter a suitable RDTM (individual read time at each wavelength).

7.4.1 Clear.

7.4.2 1.

7.4.3 Blue.

7.4.4 0.

7.5 Enter a suitable DLTM (delay time between sets of analyses).

7.5.1 Clear.

7.5.2 3.

7.5.3 Blue.

7.5.4 1.

7.6 Enter the desired ZRTM (zero time). (EXAMPLE: a ZRTM of "2" tells the instrument to purge and re-zero after every two complete anaysis cycle).

7.6.1 Clear.

7.6.2 255 (The auto-zero will not be used, so the maximum input is entered to avoid an unwanted auto-zero.).

7.6.3 Yellow.

7.6.4 Yellow.

7.7 Set PGTM (purge time). Instrument will automatically purge for input amount of time whenever the auto-zero function is triggered, or when wavelength gains or zeros are set manually. (Note.. this parameter is not being used for plant monitoring.)

7.7.1 Clear.

7.7.2 1. (sets the minimum.)

7.7.3 Blue.

7.7.4 Yellow.

7.7.5 5.

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7.8 Sets a zero intercept: (a toggle function, repeat key strokes to change).

7.8.1 Clear.

7.8.2 Blue.

7.8.3 9.

7.8.4 Instrument should print out ZR INTERCEPT. If instrument prints out NZ INTERCEPT, repeat key strokes 7.8.1-7.8.3 before proceeding.

7.9 Set printout in parts-per-million: (a toggle function).

7.9.1 Clear.

7.9.2 Blue.

7.9.3 8.

7.9.4 Instrument should print out parts-per-million. If instrument prints out PERCENT (%), repeat key strokes 7.9.1-7.9.3.

7.10 Set desired alarm level noted on instrument:

7.10.1 Clear.

7.10.2 1.

7.10.3 Blue.

7.10.4 4.

7.10.5 First component's alarm level x 10 (DCPS). Note: DCPS is the decimal shift number from the FORTRAN program. You can check the value of DCPS by performing keystrokes 7.11-7.11.3.

7.10.6 Blue.

7.10.7 Yellow.

7.10.8 4.

7.10.9 Repeat steps 7.10.5-7.10.8 for each component.

7.10.10 Note: automatic alarms are not being used. All alarm levels may be entered as 1000.

7.11 Check input of parameters.

7.11.1 Clear.

7.11.2 Yellow.

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7.11.3 PRT PARA.

7.11.4 The printout will show:

DCPS = decimal shift number, NW = number of wavelengths, NC = number of components, SCSD = scan speed (this can be any number), DLTM = delay time, RDTM = read time, ZRTM = zero time, PGTM = purge time.

7.12 Check that the wavelengths are corrected:

7.12.1 Clear.

7.12.2 Yellow.

7.12.3 PRT W.

7.13 Check that the matrix is correct:

7.13.1 Clear.

7.13.2 Yellow.

7.13.3 PRT MTRX.

7.14 Check that the alarm levels are correct:

7.14.1 Clear.

7.14.2 Blue.

7.14.3 Yellow.

7.14.4 A.

7.15 Lock memory:

7.15.1 Clear.

7.15.2 8531616.

7.15.3 Blue.

7.15.4 Blue (memory access light off).

7.16 Record the operating parameters, wavelengths, and matrix in the instrument logbook.

7.17 The instrument is now ready for operation. It needs only to be set in position and have the gains and zeroes set to be able to analyze unknowns.

NOTES: (a) If instrument power is interrupted, the cell must be purged and the instrument rezeroed.

(b) If excessive drift occurs, and the zero does not correct it, then the wavelength gains should be reset followed by re-zeroing.

(c) The parts-per-million concentrations are identified by a two character code for each of the components.

8. Plant Installation

8.1 MIRAN instrumentation will be located in necessary work areas. Several MIRAN instruments will be located in a specially built enclosure in the work areas to sample the ambient air. In addition, there will be a backup instrument in each location.

8.2 Installation of the instruments will include plumbing necessary for daily challenges using permeation generators or some suitable technique.

8.3 A separate air conditioned enclosure will house the instruments located in the control room. This is to provide a stable temperature environment, which is critical to MIRAN operation. The temperature in this enclosure should be maintained at 25 °C, ±5 °C.

8.4 When operated continuously, the source in the MIRAN burns out in approximately 3-4 months. Should this occur, the unit will not analyze samples; therefore, maintenance system must be incorporated into the daily operating procedures.

Blank

APPENDIX I

P-MATRIX SOURCE LISTING

Pages numbered 1-1 to 1-5 contain the P-Matrix program provided by Foxboro Instrument Company, Foxboro, MA. This program was modified to run on the UNIVAC 1160 mainframe. The original program supplied by Foxboro can be found in any MIRAN 80 manual. Modifications made for the study involved replacing the Hilevath statements used in the if statements and changing the values of IRD and IWR to suit the UNIVAC system.

Pages numbered I-6 and I-7 are the correct way to enter the data. These data are extracted from trial 1 (Table 4 of the main report). Data on pages I-8 and I-9 are the incorrect method of data entry. The Primary difference occurs on lines 48-54. Data entry into this program is critical because the program still provides values for the P-Matrix. Data on pages I-10 and I-11 are the result of the P-Matrix computation. Questions found on pages 1-10 and I-11 were answered in the data file.

Information found at the top of page I-11 is entered into the MIRAN 80 for automatic concentration calculations. The Miran needs the values from:

1. P-Matrix (MIRAN 80)
2. Decimal Shift Number
3. Signs follow (PLUMS)

```
@ED,R ELLZY.FORTRAN
READ-ONLY MODE
CASE UPPER ASSUMED
ED 16R1C. FRI-12/12/86-10:54:05-(11,)
EDIT
0:
      1:C
      2:C       INVERSE COEFFICIANT MATRIX CALCULATION PROGERAM,
      3:C       FOR WILKS' MODEL 80                VER. 2.0 --
      4:C
      5:C       COPYRIGHT 1976,
      6:C       WILKS SCIENTIFIC CORP.
      7:C       ALL RIGHTS RESERVED.
      8:C
      9:C       THIS PROGRAM CALCULATES A P-MATRIX BASED ON ABSORBANCE
     10:C           AND CONCENTRATION MATRICES.  IT USES THE FORMULA
     11:C           P=((B'*B)**-1)*B'.   WHERE B IS THE ABSORBANCE
     12:C           COEFFICIANT MATRIX, AND IS FOUND BY:
     13:C              B=A*C'*((C*C')**-1)
     14:C
     15:C              A PRIME (') INDICATES THE TRANSPOSE OPERATION.
     16:C
     17:C       MAJOR VARIABLES--
     18:C           NCMP=NUMBER OF COMPONENTS
     19:C           IAW=WIDTH OF A-MATRIX (=NCMP (+1 IF NON-Z INTCP))
     20:C           NLAMB=NUMBER OF WAVELENGTHS
     21:C           IPW=WIDTH OF A P-MATRIX (=NLAMB (+1 IF NON-Z INTCP))
     22:C           NSAM=NUMBER OF CALIBRATION SAMPLES
     23:C           A=ABSORBANCE MATRIX
     24:C           C=CONCENTRATION MATRIX
     25:C           P=P-MATRIX
     26:C           T=A TEMPORARY MATRIX
     27:C           ISCF=DECIMAL SHIFT COUNT FROM SCALE
     28:C
     29:C
     30:            DIMENSION TEMP(25)
     31:            DOUBLE PRECISION A(25,25),C(25,25),P(25 25),T
     32:             CHARACTER*1 K
     33:C
     34:C       IRD AND IWR SHOULD BE SET TO THE UNIT NUMBERS OF THE
     35:C          DESIRED INLPUT ANDA OUTPUT DEVICES.  (IN THIS CASE,
     36:C          BOTH DEVICES ARE NUMBER 5:  A TELETYPE IN
     37:C          OUR SYSTEM.)
     38:C
     39:            IRD=5
     40:            IWR=6
     41:            ERR=1.E-10
     42:            WRITE(IWR,1)
     43:1           FORMAT('  NUMBER OF COMPONENTS?(I2)'/)
     44:            READ(IRD,2) NCMP
     45:            WRITE(IWR,14) NCMP
     46:14          FORMAT(1X,'YOU MUST HAVE ',I3,' WAVELENTHS.'/
     47:         1 3X,'NUMBER OF WAVELENGTHS?(I2)'/)
     48:            READ(IRD,2)NLAMB
     49:2           FORMAT(I2)
     50:            WRITE(IWR,10)
     51:10          FORMAT(1X,'DO YOU WISH TO HAVE NON-ZERO INTERCEPTS'/
```

```
52:      2 3X,'IN THE CALIBRATION CURVE?')
53:           READ(IRD,11) K
54:11         FORMAT(A1)
55:           IAW=NCMP
56:           IF(K.EQ.'Y')IAW=IAW+1
57:           IPW=NLAMB
58:           IF(K.EQ.'Y') IPW=IPW+1
59:           WRITE(IWR,12)IAW
60:12         FORMAT(/,1X,'YOU MUST HAVE AT LEAST ',I4,/
61:      2 3X,'CALIBRATING SAMPLES')
62:           WRITE(IWR,13)
63:13         FORMAT(1X, 'HOW MANY SAMPLES ARE THERE?(I2)'/)
64:           READ(IRD,2) NSAM
65:           WRITE(IWR,3)
66:3       FORMAT(2X,'TYPE THE A-MATRIX(THE ABSORBANCE AT EACH WAVELENGTH'/
67:      3     'FOR THE FIRST SAMPLE,THEN SECOND SAMPLE,ETC)'/
68:      4     '(ONE PER LINE(F10.0))'/)
69:          READ(IRD,4) ((A(J,I),J=1,NLAMB),I=1,NSAM)
70:4          FORMAT(D10.0)
71:          WRITE(IWR,5)
72:5          FORMAT(2X,'TYPE THE C-MATRIX (THE CONCENTRATION OF'/
73:      1         'EACH COMPONENT FOR THE FIRST SAMPLE,ECT.)'/
74:      2         '(ONE PER LINE (F10.0))'/)
75:             READ(IRD,4) ((C(J,I),J=1,NCMP),I=1,NSAM)
76:              DO 103 I=1,NSAM
77:            C(NCMP+1,I)=1.DO
78:103           A(NLAMB+1,1)=1.DO
79:           WRITE(IWR,16)
80:16         FORMAT(//1X,'DO YOU WANT TO SEE THE INPUT MATRIX?',2X)
81:              READ(IRD,11)K
82:              IF(K .NE. 'Y')GO TO 104
83:              WRITE(IWR,17) 'HELLO'
84:17         FORMAT(//1X,'A-MATRIX--'/)
85:          DO 105 I=1,NLAMB
86:105           WRITE(IWR,9) (A(I,J),J=1,NSAM)
87:             WRITE(IWR,18)
88:18         FORMAT(//1X,'C-MATRIX--'/)
89:           DO 106 I=1,NCMP
90:106           WRITE(IWR,9) (C(I,J),J=1,NSAM)
91:C        P=C'
92:104          CALL MTRPS(C,P,IAW,NSAM)
93:C        T=C*C'
94:             CALL MMUL (C,P,T,IAW,IAW,NSAM)
95:C        T=(C*C')**-1
96:             CALL DMXINV(T,25,IAW,ERR)
97:C        C=C'*((C*C')**-1
98:             CALL MMUL(P,T,C,NSAM,IAW,IAW)
99:C        P=A*(C'*((C*C')**-1)) =B (ABSORPTION COEFFTION MATRIX)
100:            CALL MMUL(A,C,P,IAW,IAW,NSAM)
101:            WRITE(IWR,75)
102:75          FORMAT(1X,'DO YOU WISH TO SEE ABSORPTION COEFF. MATRIX')
103:            READ(IRD,11) K
104:            IF(K.NE.'Y')GO TO 20
105:            WRITE(IWR,80)
106:80          FORMAT(//1X,'ABSORPTION COEFFICIENT MATRIX',/)
107:               DO 100 I=1,IPW
108:100         WRITE(IWR,9) (P(I,J),J=1,IAW)
```

```
C      A=B' (=P' HERE)
20           CALL MTRPS(P,A,IPW,IAW)
C      T=B*B'
             CALL MMUL(A,P,T,IAW,IAW,IPW)
C      T-MATRIX IS INVERTED
             CALL DMXINV(T,25,IAW,ERR)
C      P-MATRIX =(B'*B)*B'?
             CALL MMUL(T,A,P,IAW,IPW,IAW)
             WRITE(IWR,15)
15        FORMAT(//1X,'TRUE P-MATRIX-- (UNSCALED)'/)
             DO 901 I=1,NCMP
901          WRITE(IWR,9) (P(I,J),J=1,IPW)
9            FORMAT(1P6D12.3,(6X,5D12.3))
             CALL SCALE(P,NCMP,IPW,ISCF)
             WRITE(IWR,6)
6         FORMAT(//1X,'P-MATRIX (FOR "80")--')
             DO 101 I=1,NCMP
             DO 102 J=1,IPW
102             TEMP(J)=DABS(P(I,J))
101       WRITE(IWR,7) (TEMP(J),J=1,IPW)
7         FORMAT(10F7.0)
          WRITE(IWR,8) ISCF
8         FORMAT(/1X,'DECIMAL SHIFT NUMBER=',I4)
             CALL PLUMS(P,NCMP,IPW)
             STOP
             END
C
C    ALL SUBROUTINES FOLLOW
          SUBROUTINE MMUL(A,B,C,NR,NC,NM)
C
C
C      THIS ROUTINE SETS C=A*B
C
C      NR=NUMBER OF ROWS IN A
C      NC=NUMBER OF COLUMNS IN B
C      NM=NUMBER OF COLUMNS IN A AND NUMBER OF ROWS IN B
C
C
          DOUBLE PRECISION A(25,25),B(25,25),C(25,25),T
          DO 101 IR=1,NR
          DO 101 IC=1,NC
          T=0.0
             DO 102 K=1,NM
102          T=T+A(IR,K)*B(K,IC)
101       C(IR,IC)=T
          RETURN
          END
C
C
          SUBROUTINE DMXINV(A,N,M,ERR)
C
C
C      THIS ROUTINE INVERTS T IN PLACE
C
C      N=SIZE OF ARRAY (SQUARE)
C      M=SIZE OF T (IN UPPER LEFT CORNER OF ITS ARRAY)
C      ERR=ERROR PARAMETER TO TEST FOR FAILURE OF INVERSION
```

```
C           (SINGULARITY)
C
C
           DOUBLE PRECISION A(1),X
           INTEGER II,J
           IWR=6
            DO 1 I=1,M
               II=I+N*(I-1)
               X=A(II)
               A(II)=1.0
           IF(DABS(X) .LE. ERR) GO TO 5
               DO 2 J=1,M
               IJ=I+N*(J-1)
2          A(IJ)=A(IJ)/X
               DO 1 K=1,M
               IF(K-I) 3,1,3
3              KI=K+N*(I-1)
               X=A(KI)
               A(KI)=0.0
               DO 4 J=1,M
               KJ=K+N*(J-1)
               IJ=I+N*(J-1)
4               A(KJ)=A(KJ)-X*A(IJ)
1          CONTINUE
           RETURN
5          WRITE (IWR,9)
9          FORMAT('  ',/'***DIANGONAL ZERO,TRY DIFFERENT METHOD**')
           END
C
C SECOND SUBRCUTINE
           SUBROUTINE SCALE(P,NCMP,IPW,ISCF)
C
C
C       THIS ROUTINE SCALES THE P-MATRIX
C
C       IT MULTIPLIES BY 6.5536 TO PUT IT IN A SUITABLE FORM
C           FOR THE "80".  THEN IT MULTIPLIES OR DIVIDES BY
C           A POWER OF 10 TO GET THE NUMBERS AS CLOSE TO 65536
C           AS POSSIBLE, RETURNING THE DECIMAL SHIFT
C           COUNT IN "ISCF"
C
C
           DOUBLE PRECISION P(25,25)
           BIG=DABS(P(1,1))*6.5536
           DO 101 I=1,NCMP
              DO 101 J=1,IPW
              P(I,J)=P(I,J)*6.5536
              IF(DABS(P(I,J)) .GT. BIG) BIG=DABS(P(I,J))
101        CONTINUE
           AK=ALOG10(BIG)-4.816479
           IF(AK .GE. 0)AK=AK+1.0
           K=AK
           SCF=10.0**K
              DO 102 I=1,NCMP
              DO 102 J=1,IPW
102           P(I,J)=P(I,J)/SCF
              ISCF= -K
```

```
223:              IF(ISCF .LT. 0)ISCF=ISCF+128
224:            RETURN
225:            END
226:C
227:C THIRD SUBROUTINE
228:            SUBROUTINE PLUMS(P,NCMP,IPW)
229:C
230:C
231:C       THIS ROUTINE EXTRACTS THE SIGNS FROM THE P-MATRIX,
232:C           AND PUTS THEM IN A SUITABLE FORM FOR THE "80".
233:C
234:C
235:              DOUBLE PRECISION P(25,25)
236:            IWR=6
237:            WRITE(IWR,1)
238:1           FORMAT(1X,'SIGNS FOLLOWS---')
239:            IPC=1
240:            IP=0
241:                  DO 101 I=1,NCMP
242:                  DO 101 J=1,IPW
243:                   IB=0
244:                  IF(P(I,J) .LT. 0.0)IB=1
245:                  IP=IP+IB*IPC
246:                  IPC=IPC*2
247:                  IF(IPC .NE. 256) GO TO 101
248:                  WRITE(IWR,2)IP
249:2                 FORMAT(1X,I4)
250:                  IPC=1
251:                  IP=0
252:101               CONTINUE
253:                  WRITE(IWR,2) IP
254:             RETURN
255:             END
256:C
257:C  FOURTH SUBROUTINE
258:C
259:            SUBROUTINE MTRPS(A,B,NR,NC)
260:C
261:C
262:C       THIS ROUTINE TRANSPOSES A INTO B:  B=A'
263:C
264:C       NR=NUMBER OF ROWS IN A
265:C       NC=NUMBER OF COLUMNS IN A
266:C
267:C
268:            DOUBLE PRECISION A(25,25),B(25,25)
269:                  DO 101 I=1,NR
270:                  DO 101 J=1,NC
271:101               B(J,I)=A(I,J)
272:            RETURN
273.            END
EOF:273
0:
END ED. NO CORRECTIONS APPLIED
```

```
@ED,R ELLZY.TRIAL
READ-ONLY MODE
CASE UPPER ASSUMED
ED 16R1C. FRI-12/12/86-10:54:53-(0.)
EDIT
0:
       1:@XQT
       2:02
       3:06
       4:N
       5:06
       6:.0008
       7:.0010
       8:.0008
       9:.0006
      10:.0008
      11:.0005
      12:.0018
      13:.0025
      14:.0025
      15:.0026
      16:.0017
      17:.0009
      18:.0027
      19:.0035
      20:.0037
      21:.0041
      22:.0021
      23:.0009
      24:.0010
      25:.0003
      26:.0004
      27:.0004
      28:.0024
      29:.0006
      30:.0019
      31:.0005
      32:.0005
      33:.0007
      34:.0064
      35:.0010
      36:.0031
      37:.0011
      38:.0011
      39:.0015
      40:.0107
      41:.0020
      42:.52
      43:1.56
      44:2.60
      45:0.
      46:0.
      47:0.
      48:0.
      49:0.
      50:0.
      51:.425
      52:1.275
      53:2.125
      54:Y
      55:Y
EOF:55
0:
END ED. NO CORRECTIONS APPLIED
```

```
*ED,R ELLZY.2TRIAL
READ-ONLY MODE
CASE UPPER ASSUMED
ED 16R1C. FRI-12/12/86 10.55:12-(1,)
EDIT
O:
       1:*XQT
       2:02
       3:06
       4:N
       5:06
       6:.0009
       7:.0010
       8:.0008
       9:.0006
      10:.0008
      11:.0005
      12:.0018
      13:.0025
      14:.0025
      15:.0026
      16:.0017
      17:.0009
      18:.0027
      19:.0035
      20:.0037
      21:.0041
      22:.0021
      23:.0009
      24:.0010
      25:.0003
      26:.0004
      27:.0004
      28:.0024
      29:.0006
      30:.0019
      31:.0005
      32:.0005
      33:.0007
      34:.0064
      35:.0010
      36:.0031
      37:.0011
      38:.0011
      39:.0015
      40:.0107
      41:.0020
      42:.52
      43:1.56
      44:2.60
      45:0
      46:0.
      47:0.
      48:.425
      49:1.275
      50:2.125
      51:0.
      52:0.
      53:0.
      54:0.
      55:Y
      56:Y
EOF:56
O:
END ED. NO CORRECTIONS APPLIED
```

```
*MAP
Collector 31R2 (840425 1811:06) 1986 Dec 12 Fri 1055:28
START*006420. PROG SIZE(I/D)*3676/6995
END MAP.  ERRORS. 0  TIME: 16.945  STORAGE: 17122/9/034077/0110577


*XQT
 NUMBER OF COMPONENTS?(I2)

YOU MUST HAVE    2 WAVELENGTHS.
  NUMBER OF WAVELENGTHS?(I2)

DO YOU WISH TO HAVE NON-ZERO INTERCEPTS
  IN THE CALIBRATION CURVE?


YOU MUST HAVE AT LEAST     2
  CALIBRATING SAMPLES
HOW MANY SAMPLES ARE THERE?(I2)

 TYPE THE A-MATRIX(THE ABSORBANCE AT EACH WAVELENGTH
OR THE FIRST SAMPLE,THEN SECOND SAMPLE,ETC)
ONE PER LINE(F10.0))

 TYPE THE C-MATRIX (THE CONCENTRATION OF
ACH COMPONENT FOR THE FIRST SAMPLE,ECT.)
ONE PER LINE (F10.0))


DO YOU WANT TO SEE THE INPUT MATRIX?


A MATRIX--

  8.000-004   1.800-003   2.700-003   1.000-003   1.900-003   3.100-003
  1.000-003   2.500-003   3.500-003   3.000-004   5.000-004   1.100-003
  8.000-004   2.500-003   3.700-003   4.000-004   5.000-004   1.100-003
  6.000-004   2.600-003   4.100-003   4.000-004   7.000-004   1.500-003
  8.000-004   1.700-003   2.100-003   2.400-003   6.400-003   1.070-002
  5.000-004   9.000-004   9.000-004   6.000-004   1.000-003   2.000-003


C-MATRIX--

  5.200-001   2.600+000     .000        .000        .000      1.275+000
  1.560+000     .000       .000        .000      4.250-001   2.125+000
DO YOU WISH TO SEE ABSORPTION COEFF. MATRIX


ABSORPTION COEFFICIENT MATRIX

  3.064-003   4.963-003
  1.251-003   6.844-004
    .000        .000
    .000        .000
    .000      4.250-001
```

```
  1.275+000   2.125+000


TRUE P-MATRIX-- (UNSCALED)

 -1.490 002  -3.847-003     .000         .000       -7.083-001  -6.299+000
  1.007-002   2.770-003     .000         .000        4.250-001   4.250+000


P-MATRIX (FOR "80")--
   98.     25.      0.      0.  4642. 41281.
   66.     18.      0.      0.  2785. 27853.

DECIMAL SHIFT NUMBER=   3
SIGNS FOLLOWS---
  51
   0


@XQT
 NUMBER OF COMPONENTS?(I2)

YOU MUST HAVE   2 WAVELENTHS.
  NUMBER OF WAVELENGTHS?(I2)

DO YOU WISH TO HAVE NON-ZERO INTERCEPTS
  IN THE CALIBRATION CURVE?


YOU MUST HAVE AT LEAST    2
  CALIBRATING SAMPLES
HOW MANY SAMPLES ARE THERE?(I2)

 TYPE THE A-MATRIX(THE ABSORBANCE AT EACH WAVELENGTH
OR THE FIRST SAMPLE,THEN SECOND SAMPLE,ETC)
ONE PER LINE(F10.0))

 TYPE THE C-MATRIX (THE CONCENTRATION OF
ACH COMPONENT FOR THE FIRST SAMPLE,ECT.)
ONE PER LINE (F10.0))



DO YOU WANT TO SEE THE INPUT MATRIX?
DO YOU WISH TO SEE ABSORPTION COEFF. MATRIX


ABSORPTION COEFFICIENT MATRIX

  9.790-004   1.420-003
  8.149-004   9.952-004
   .000         .000
  4.250-001   1.275+000
  2.125+000    .000
   .000        .000
```

```
TRUE P-MATRIX-- (UNSCALED)

  3.157-005   4.785-005     .000      -6.228-002   4.242-001     .000
  1.533-003   1.089-003     .000       1.324+000   2.452-001     .000


P-MATRIX (FOR "80")--
    0.      0.      0.    408.   2780.      0.
   10.      7.      0.   8677.   1607.      0.

DECIMAL SHIFT NUMBER=   3
SIGNS FOLLOWS---
   8
   0
DATA IGNORED - IN CONTROL MODE
```